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# Synthetic Protein Fibers from Protein-Detergent Complexes

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THIS discussion will deal with potentially useful plastic properties imparted to proteins by long-chain hydrocarbon salts such as alkyl sulfonates, sulfates, or phosphates, and with methods by which such agents, commonly referred to as detergents, make it possible to manipulate various types of proteins into fibrous forms. The detergents can then be recovered following such manipulation, leaving the regenerated protein in the oriented fibrous state [1, 2].

First, however, we shall consider the reasons for seeking to make fibers from proteins.

First of all, the common natural protein fibers have desirable characteristics. We find in wool, silk, and hair such properties as warmth, durability, resilience, and high affinity for dyes. It is probable that synthetic protein fibers can be made that have similar desirable characteristics and possibly others not found in the natural fibers. Also, as with cellulose, there is the possibility of developing methods for reconstruction of the natural protein fibers into fibers having new and specialized uses.

Another reason why we seek to make fibers from proteins is the abundance of available raw materials. A few are wastes; some have little value; others have moderate or high value. Many of the more common proteins, such as casein, soybean protein, zein, wheat gluten, cottonseed protein, peanut protein, alfalfa protein, chicken feathers, and technical egg white, are being investigated as possible raw materials for synthetic fibers.

Much of this discussion will deal with technical egg white and in particular with egg albumin, which comprises about 70 percent of dry egg white and which is easily prepared in crystalline form for investigational work. The general principles that we will discuss appear to be applicable to other proteins as well. For example, much of the same treatment used with egg albumin is applicable to the preparation of fibers from chicken-feather keratin, from dispersed horn, hoof, and wool, from blood fibrinogen, and from others. Description of the preparation of fibers from egg white and feather proteins will be given in this paper.

## Theoretical Considerations

### *1. General*

Fundamental considerations indicate that proteins have a structure that is appropriate for fibers. The

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TABLE I. POLAR GROUPS OF EGG ALBUMIN

| Group | Number per molecule of 45,000 M.W. |
|---|---|
| Basic: | |
| Imidazole (=NH) | 4 |
| ε-amino ($-NH_2$) | 24 |
| Guanidine $\left(\begin{matrix} H & NH \\ | & || \\ -N-C- & NH_2 \end{matrix}\right)$ | 15 |
| Total basic groups | 43 |
| Acidic: | |
| Free carboxylic acid (—COOH) | 51 |
| Phosphoric acid $\left(\begin{matrix} O \\ || \\ -O-P- \\ | \\ OH \end{matrix}\right)$ | 1 |
| Phenolic (—OH) | 9 |
| Sulfhydryl (—SH) | 6 |
| Total acidic groups | 67 |
| Disulfide (—S—S—) | 3 |
| Amide $\left(\begin{matrix} -C-NH_2 \\ || \\ O \end{matrix}\right)$ | 36 |

classical conception of Fischer, that proteins are essentially chains of amino acids joined by the peptide linkage, is the foundation of our present knowledge of protein structure (Figure 1).

We know that a single protein molecule may consist of a chain of several hundred amino acid residues, including residues of 10 to 25 different amino acids, and we know that a close relation exists between the strength of fibers and the length of the constituent chains. We also know that chain molecules are the basis for strength and elastic properties in many high polymers. Figure 2 show a portion of the protein chain, in comparison with sections of the chains of natural rubber and nylon.

The problem with protein fibers, as with regenerated cellulose, is to liberate the chains from their natural confinements and to reconstruct them into fibers having desirable properties. If we are to take maximum advantage of the proteins available, it is of utmost importance that we preserve as much of their natural chain length as possible. We must therefore choose conditions that will not lead to rupture of the main valence chain.

### *2. Polar Groups of Egg Albumin*

One of the most characteristic properties of proteins, which distinguishes them from many other high-polymer systems, is the number of highly active polar groups distributed along the main chain. These groups are attached to the side chains of the amino acid residues. Because of these groups and because of free rotation around single bonds, we find proteins in various structural and chemical combinations. These combinations are found in varying sizes and solubilities, in elongated and folded configuration, and in complexes with pigments, fats, carbohydrates, or other proteins. Several of the various types of bonds that are possible between the polar elements of individual protein chains and those of adjacent chains are shown in Figure 2. The number, distribution, and character of such bonds determine to a large degree the physical behavior of protein fibers.

A tabulation of the number of various active side-chain groups in egg albumin is shown in Table I.

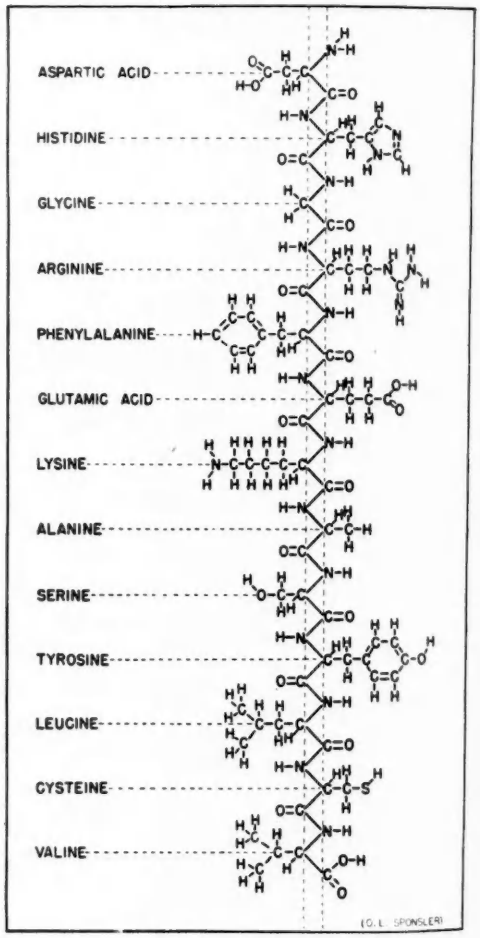



FIG. 1. *Chain structure of proteins formed by condensation of α-amino acids. Free polar groups are located laterally along chain.*

These data are based on the best analyses available and are calculated with 45,000 as the molecular weight of egg albumin. Of particular interest for this discussion are the 43 basic groups, which include the imidazole group of histidine, the guanidine group of arginine, and the $\epsilon$-amino group of lysine. Interactions involving these groups will be referred to later on in this discussion. It will be shown that the primary interaction of proteins with long-chain hydrocarbons is analogous to the interaction of proteins with dyes; the basic groups interact by ionic exchange with anionic detergent salts and the acidic groups with cationic salts. It will be shown that such interactions are conditioned by the structure of the protein as well as by the structure of the organic salt with which the protein interacts. A secondary combination of detergent occurs, which determines the unique flow properties given to proteins by treatment with long-chain salts.

### 3. *Size and Shape of Egg Albumin*

Some of the structural properties of egg albumin are listed in Table II. The number of amino acid residues, calculated from the value reported by Chibnall [3] for average residue weight, is around 400. Accordingly, the length of the peptide chain of egg albumin, if completely unfolded and considered as a single chain, would be about 1,400 Å. if we use 3.5 Å.

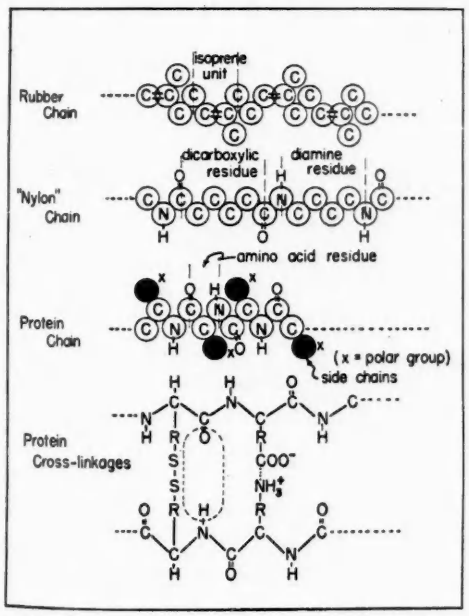



FIG. 2. *Protein chains compared with chains of natural rubber and nylon, showing location of polar groups in protein and some of the cross-linkages that can form.*

TABLE II. STRUCTURAL PROPERTIES OF EGG ALBUMIN

| |
|---|
| Molecular weight = 45,000 |
| Average amino acid residue weight = 111.4 |
| Number of residues (D.P.) = $\frac{45{,}000}{111.4}$ = 404 |
| Total length (calculated as 1 chain) = 404 × 3.5 Å. = 1,414 Å. |
| Total length (calculated as 4 chains) = $\frac{1{,}414}{4}$ = 354 Å. |
| Cross section of single chain (x-ray) = 9.5 Å. |

as the length of each peptide unit along the chain. It has been suggested that there may be as many as 4 chains in each egg-albumin molecule. If this is true and if these are assumed to be of equal length, each would approximate 350 to 360 Å. in length, and since the cross section of a peptide chain is about 9 to 10 Å., the ratio of length to width for each chain would be about 36 to 1. Offhand, such a chain would not appear to be suitable for fiber formation [4, 5].

But native egg albumin in solution does not behave as a highly asymmetrical molecule. Ultracentrifugal sedimentation, diffusion, and viscosity studies indicate that the ratio of major to minor axes of the molecule may be 4 to 1 or less; in other words, egg albumin does not deviate greatly from the spherical shape and, therefore, may be regarded as having a folded corpuscular structure. Obviously this form of the protein is not desirable for fiber formation.

### 4. *Denaturation and Unfolding of Proteins*

A distinguishing feature of egg albumin and of other truly corpuscular proteins is the ease with which they undergo denaturation. Denaturation can be induced by a variety of agents, including heat, alkali, urea, organic solvents, and surface forces. Of particular interest for this discussion is the fact that detergents can cause denaturation, as first shown by Anson [6].

Denaturation is generally characterized by loss of specific properties in biologically active proteins, by loss of crystallizability in crystallizable proteins, and by the appearance of characteristics of fibrous molecules under certain conditions. Where native proteins appear to have regularly folded configurations, this regularity is lost on denaturation.

In certain environments denaturation may also in-

volve a change in size of the molecule. Alkaline media, urea, and also solutions containing long-chain hydrocarbon salts can cause dissociation of certain proteins. Insulin, for example, is dissociated into half size by dodecyl sulfate [7]. In addition to causing dissociation, alkalies can cause hydrolytic cleavage of the main peptide chain; secondary reactions of this sort are to be avoided if maximum strength in synthetic fibers is to be attained.

When denaturation is accompanied by indications of unfolding of the molecule, the chains appear to return to the more spherical form if the environmental influences are removed. The protein then lacks the specific properties of the original native protein and the chains are assumed to be folded into a random configuration. A restraining force thus appears to be necessary in order to keep the chains extended. This restraining force may result from the close proximity of protein molecules in concentrated solutions. For example, Figure 3 shows the ultracentrifugal sedimentation patterns for the normal folded form of the native protein thyroglobulin (on the right) and an unfolded configuration of the same protein relative stabilized by the concentrated solution (on the left) [8, 9]. Because of increased frictional resistance to movement in solution, the unfolded form sediments at a slower rate than the folded form. The unfolding in this case has been caused to occur by allowing the pure protein to stand in an electrolyte-free condition in a concentrated solution for a period of time. It would appear that interchain electrostatic forces are concerned in the unfolding and are sufficient to overcome the elastic forces of the peptide chains that tend to curl the chains into the more probable configuration. When the restraining force is removed (for example, by addition of electrolyte, by dilution, or by heating) the protein again sediments at a rate normal for the folded form even though it is denatured by heating.

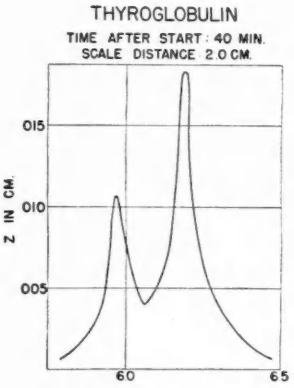



FIG. 3. *Ultracentrifugal sedimentation diagram of thyroglobulin protein, showing 2 forms. Peak to right corresponds to gradient of normal folded protein; peak to left, to unfolded form, sedimenting slower by virtue of increased frictional resistance.*

The restraint necessary to keep protein chains unfolded may be the confinement of the molecules on a surface. A most revealing experiment that illustrates the unfolding of a protein on a surface was carried out by Astbury *et al.* [10], who spread egg albumin into a film which they found to measure 9 to 10 Å. in thickness, corresponding to the backbone width of fibrous proteins as measured by x-ray diffraction.

The restraint favoring unfolded chains may be supplied by appropriate chemical agents, such as urea or synthetic detergents. In concentrated urea solution, many proteins exhibit enhanced viscosity, consistent with the view that the protein chains have unfolded. But when the urea is removed by dialysis the proteins again behave as if they were highly folded [11]. The effects of detergents on proteins are somewhat

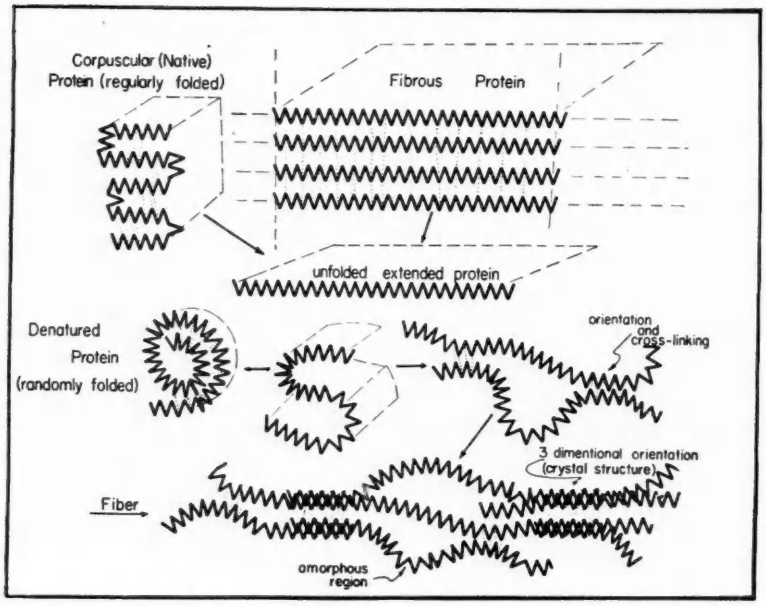



FIG. 4. *Representation of structural transformations involved in fiber formation from corpuscular and fibrous proteins. In corpuscular proteins chains are restrained in regularly folded configurations; in fibrous proteins they are restrained in extended configuration. In fibers, portions of chains are restrained in extended configuration.*

similar to those of urea and will be discussed later in this paper.

While all of these considerations have been discussed in regard to the so-called corpuscular proteins, they apply to the natural fibrous proteins as well. Such materials, including the keratins of feathers, wool, horn, and hoof, are restrained in their natural state in extended configurations. But when the chains are freed by chemical reduction of the disulfide bonds they, too, behave as do the chains of the corpuscular proteins and curl up to more probable configurations.

To summarize: The main problem in making fibers from proteins consists in the liberation of chains from their natural confinements and in the unfolding and restraining of chains in an elongated form until new cross-linkages can be set up. These aspects are protrayed in Figure 4.

Several kinds of protein dispersions have been used in making fibers. At present, commercial casein and soybean fibers are made from concentrated dispersions of these proteins in alkali, by extrusion through spinnerets into acid coagulating baths.

Astbury [12] has used concentrated dispersions of corpuscular proteins in urea, a known solvent and denaturant for proteins, with precipitation by acid. Von Weimarn [13] has dispersed silk in concentrated solutions of electrolytes such as lithium chloride and then regenerated it.

Present-day artificial commercial fibers made of protein lack the structural qualities necessary for a high degree of strength. Eventually methods may be perfected that will make possible the commercial production of protein fibers at least as good as the natural protein fibers. One requirement is a protein chain of appropriate length; another is an effective means of handling the protein. Eventually various techniques

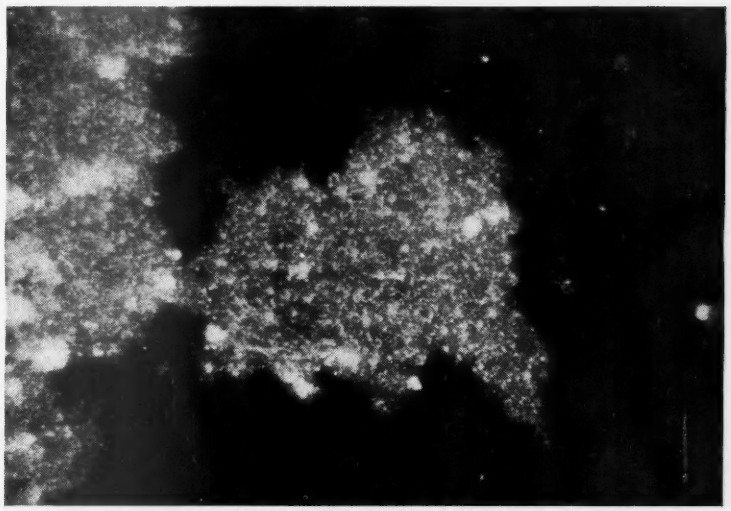


FIG. 5. *Floccules precipitated by dehydration from dilute protein-detergent solutions (magnification 630 ×).*

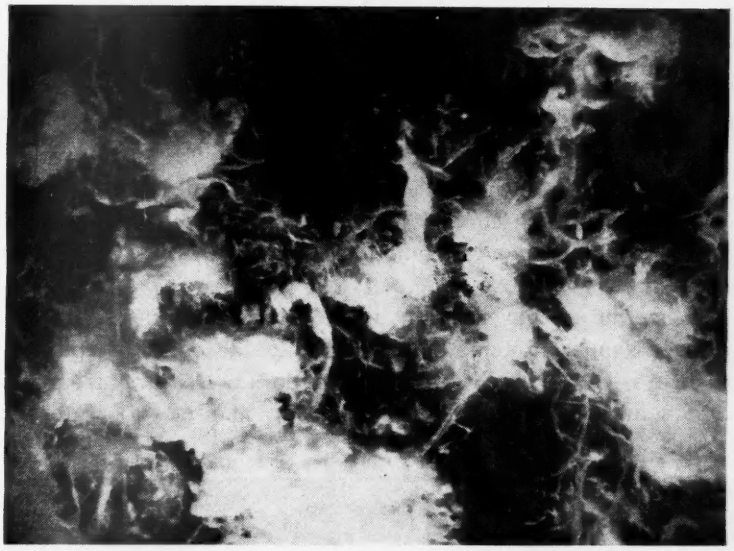


FIG. 6. *Fibrils precipitated by dehydration agents from concentrated protein-detergent solutions (magnification 3.5 ×).*

FIG. 7. *Electron microscopic photograph of fibril precipitated from protein-detergent solution showing bundle structure and fibril cleavage (magnification 4,000 ×).*

may be perfected, each having special adaptabilities. This problem is receiving attention by numerous research groups at the present time [14, 15, 16].

We are considering the use of synthetic detergents as agents for making protein fibers, not only because these agents are known to be excellent solvents and denaturants for proteins, but also because they are mild in comparison with alkalies and, in addition, they contribute, as we shall see, unique flow properties to the protein.

Detergents are relatively cheap and, of course, may become even less expensive. Recovery of the detergent in usable form after each cycle in fiber spinning may also prove to be economically feasible.

*5. Protein-Detergent Systems*

*a. Viscosities of Solutions and Properties of Precipitates.* When an anionic detergent such as a long-chain sulfonate or sulfate is added to a protein on the acid side of the protein isoelectric point, precipitation of the protein may occur directly. Harris, Steinhardt, and their coworkers [17] have compared the affinities of wool and egg albumin (on the acid side of the protein isoelectric point) for the anions of a series of acids including long-chain sulfuric acids. They found a high affinity of these proteins for the long-chain anions, and the affinity increases with increase in size of the anion.

When an anionic detergent is added to egg albumin or similar proteins on the alkaline side of the protein isoelectric point, precipitation does not occur and solutions exhibiting high viscosity and other characteristic properties may be obtained. Such concentrated solutions exhibit viscosities much greater than that of either the protein or the detergent alone under similar conditions and exhibit flow birefringence that is characteristic of higher asymmetric particles, whereas the protein or detergent alone does not show this behavior.

The dilute solutions of such mixtures of protein and detergent, however, do not have much greater viscosities than solutions of similar concentrations of the protein alone. If such dilute solutions are treated with a dehydrating agent such as acetone, the protein will separate in the floccular form shown (enlarged) in Figure 5. On the other hand, if the concentrated solutions, showing high viscosity and flow birefringence, are dehydrated by acetone, the protein will separate in fibrous form, as shown (enlarged) in Figure 6. That this latter precipitate is truly fibrous down to and approaching molecular dimensions is shown by electron-microscopic photographs of the separated fibers. The bundle structure and fibrous cleavage of the material are clearly evident in Figure 7. The smallest visible fibers measure 500 to 700 Å. in width; hence they are composed of numerous protein chains. These experiments clearly indicate that the kinetic units of the concentrated solutions are of an extended-chain character. When treated with electrolytes, both the dilute and concentrated solutions of protein-detergent mixtures yield stringy precipitates. Under these conditions the precipitate from the dilute solution is first flocculent, but the water present permits the precipitated particles to flow together, to yield a stringy mass.

Figure 8 shows the character of the precipitate that can be obtained from such widely differing proteins as native or heat-denatured egg albumin and feather keratin, by treatment with an alkylbenzene sulfonate, followed by precipitation with an electrolyte. Ordinarily these proteins will precipitate from solution in a floccular form, showing little cohesion.

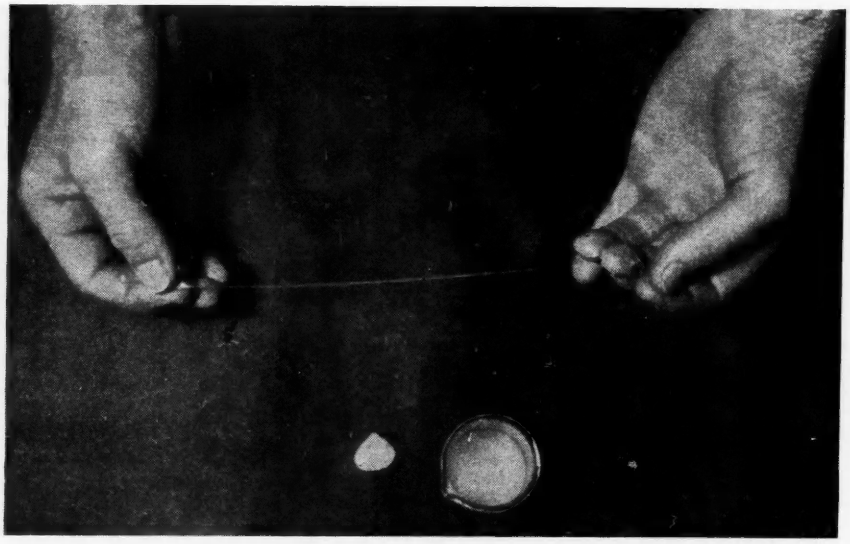


FIG. 8. *Flow property of proteins precipitated by electrolyte from detergent solution.*

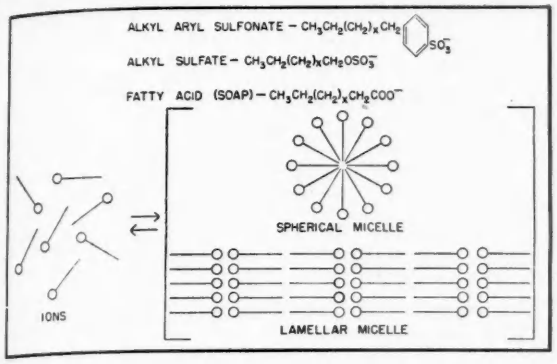



FIG. 9. *Summary of structural properties of organic detergents (long-chain hydrocarbon salts). The separate ions present in dilute aqueous solution appear to associate to give spherical or lamellar micelles in moderate or concentrated solution.*

but, as seen, the treatment, followed by precipitation by electrolyte, yields a slimy precipitate that flows under stress and forms fibers. These protein and detergent mixtures in concentrated viscous solutions are readily extruded through standard spinnerets into salt coagulating baths to form fibers which can be oriented under proper conditions. When dried, the unoriented fibers become brittle, thus indicating that water is essential for flow. The molecular aspects of this behavior will be discussed first.

This ability to change proteins to a plastic state favorable to fiber formation is characteristic of the salts of various anionic detergents, including sulfates, sulfonates, and the phosphates, but not of ordinary carboxy soaps. This behavior is also characteristic of cationic detergents such as substituted pyridinium chlorides.

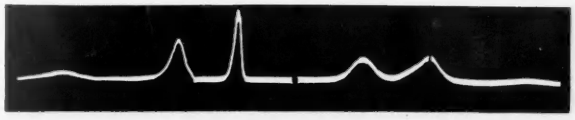
A non-ionic detergent such as a polyether alcohol is not effective. Sulfonates of lower molecular weight, such as sodium benzene sulfonate and sodium naphthalene sulfonate, are not effective, thus indicating that plus or minus attraction does not account for all of the effects observed. It is significant that the lower-weight sulfonates also lack the colloidal behavior shown by long-chain compounds. With the addition of an isopropyl chain on naphthalene sulfonate, the detergent properties appear and the characteristic effects with egg albumin are observed.

The character of the precipitates obtained by salting out from solutions varies with the proportions of protein and detergent in the mixture. With egg albumin and sodium dodecylbenzene sulfonate, for example, the precipitate formed is flocculent when the proportion of protein is high. As the proportion of detergent is increased, the precipitates become increasingly slimy.

*b. Electrophoretic Behavior of Egg Albumin and Alkylbenzene Sulfonates.* Examination of the solutions of mixtures of albumin and sodium dodecylbenzene sulfonate * by electrophoresis is particularly revealing [18]. Egg albumin, by itself, exhibits a well-defined electrophoretic boundary. Its mobility in phosphates at pH 6.5 and ionic strength 0.1 is

FIG. 10. *Electrophoretic diagrams of mixtures of egg albumin and alkylbenzene sulfonate. The total protein plus detergent concentration was 1 percent; pH = 6.5; $\mu = 0.1$; $t = 0.75°$ C.*

Ascending Boundaries→ | ←Descending Boundaries



3 2 1 1 2 3

*90:10 Native Protein-Detergent*
*Boundaries: (1) protein-detergent complex; (2) excess native protein; (3) delta and epsilon boundaries.*

2 1 1 2

*60:40 Native Protein-Detergent*
*Boundaries: (1) protein-detergent complex; (2) delta and epsilon boundaries.*

3 2 1 1 2 3

*10:90 Native Protein-Detergent*
*Boundaries: (1) free detergent; (2) protein-detergent complex; (3) delta and epsilon boundaries.*

1 1

*90:10 Heat-Denatured Protein-Detergent*
*Boundaries: (1) protein-detergent complex; (2) delta and epsilon boundaries were too small to be seen.*

* Experiments performed with pure decyl- and dodecylbenzene sulfonates give essentially the same results as those performed with the alkylbenzene sulfonates of commerce. The latter may consist of chains ranging from 5 to 20 atoms, although averaging in the neighborhood of decyl or dodecyl. The commercial mixtures can be freed of contaminating inorganic salts by extraction with absolute alcohol.

$-5.5 \times 10^{-5}$ cm./sec./volt/cm. Sodium dodecylbenzene sulfonate under similar conditions shows a more complex boundary having an average mobility of $-20 \times 10^{-5}$. When a 1-percent solution of egg albumin and a similar solution of sodium alkylbenzene sulfonate are mixed, at a pH alkaline to the protein isoelectric point, combination apparently takes place, even though both the protein and the detergent have a similar sign of net charge. This combination is inferred from the appearance of a new boundary having a mobility between that of the protein and that of the detergent. The extent to which the protein and the detergent combine can be determined from measurements of the areas of the peaks corresponding to the concentration gradients. From measurements of this sort it is found that the compositions of the complexes vary according to the ratio in which the protein and the detergent are mixed, and that the total amount of detergent that can be bound by the protein is considerably in excess of that corresponding to stoichiometric interaction of the long-chain salts with the basic groups of the protein.

Much of our present knowledge of long-chain hydrocarbon salts is based on the work of McBains, Hartley, Lottermosser, Hess, Thiessen, and Tartar. Certain of the structural aspects of these colloidal electrolytes are summarized in Figure 9. In highly dilute solutions, long-chain hydrocarbon salts behave as single ions, as shown by measurements of conductivity and osmotic coefficient. In more concentrated solutions (including concentrations used in all of the experiments reported here) detergents undergo association into micelles having colloidal dimensions. Two forms are believed to be present: the spherical micelle, which may contain as many as 40 to 50 ions, and the lamellar structure, evidence for which is obtained through x-ray measurements showing characteristic identity periods corresponding to the layer structure shown in Figure 9.

Figure 10 represents exposures made at given times on electrophoretic runs on 1-percent mixtures of native and denatured egg albumin and sodium dodecylbenzene sulfonate in various ratios. The portions of the diagrams to the left of the center represent the rising boundaries of the U-shaped electrophoresis cell, and those to the right represent the descending boundaries. In the photographs the boundaries move toward the center. The upper line represents the gradients for a mixture of native egg albumin and sulfonate under conditions in which there is an excess of the protein. In this case 90 parts of the native protein were mixed with 10 parts of the sulfonate. The pH was 6.5 and the ionic strength 0.1. Neglecting the small so-called epsilon and delta boundaries located at the extreme left and right, which are essentially salt gradients and are not of significance for this discussion, we observe that two migrating boundaries are present. The faster of the two main boundaries has a mobility between that of the native protein and that of the detergent, and represents a combination product. The slower boundary, having mobility corresponding to that of native egg albumin, appears to be excess native protein. No free-detergent boundary is seen. An analysis of the areas of the peaks indicates that the composition of the complex is approximately 3 parts by weight of protein to 1 of detergent. On an ionic basis this proportion corresponds to a ratio of one detergent ion to each basic group of the protein, and it would appear that under these conditions the reaction between native protein and detergent is stoichiometric and of electrostatic nature, involving the separate detergent ions.

The second line in Figure 10 represents the gradients found for a mixture of native protein and sodium dodecylbenzene sulfonate made with a greater pro-

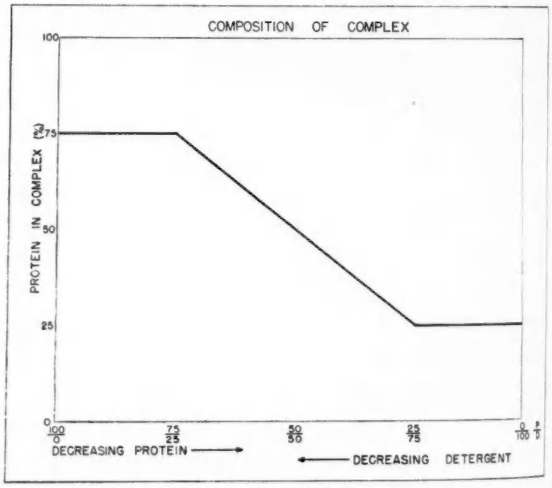



FIG. 11. *Variation of protein in complex with proportion by weight of native egg albumin and dodecylbenzene sulfonate used in mixtures. The region of constant proportion (3 to 1 by weight: protein to detergent) at upper left corresponds to a ratio of 1 detergent ion for each basic group. The region of constant composition at lower left (1 to 3) corresponds to about 9 detergent ions for each basic group. In between, at 1:1, complexes have desirable flow properties for making fibers.*

portion of detergent to protein in this case—60 parts by weight of protein to 40 parts of the detergent. No free protein or detergent boundary is seen, all of the protein being combined with all of the detergent added. Under these conditions the amount of detergent bound by the protein exceeds that which would be bound by stoichiometric proportion. Complexes having this proportion have the flow properties that are favorable for the making of fibers.

The third line in Figure 10 represents the gradients for a mixture of native protein with excess of the dodecylbenzene sulfonate. In this case the mixture was made with 90 parts by weight of detergent to 10 parts of protein. A free boundary that migrates faster than the complex is observed, and this appears to be free detergent. No free protein boundary is seen. The composition of the complex in this mixture, as determined from analysis of areas of the peaks, approximates 3 parts by weight of detergent to 1 part of protein and represents the maximum combining capacity of the protein for the detergent. This combination is of the order of 9 detergent ions for each basic group. The lowest line shows the gradients obtained with a mixture of excess heat-denatured egg albumin and sodium dodecylbenzene sulfonate. The proportions were the same as with the excess native protein—namely, 90 parts of protein to 10 of detergent. In this case, in contrast to the behavior found with the mixture of native protein in this proportion, all of the detergent was distributed over all of the protein and only one boundary is seen. With higher proportions of detergent, the behaviors of the native and the heat-denatured albumins are similar.

Good agreement was obtained between the data on compositions from electrophoretic analyses and those from nitrogen analyses of the salt-precipitated complexes.

The results of the study of composition of the complex as a function of mixing ratio of protein to detergent are summarized in Figure 11. The ordinate represents percentage of albumin in the complex, and the abscissa represents the composition of the mixtures. It is seen that the composition of the complexes remains essentially constant at about 75 percent albumin and 25 percent detergent by weight, or 3 to 1, as long as mixtures made with native albumin contain more than 3 parts by weight of protein per unit of detergent used. This composition, as previously stated, corresponds to an apparent stoichiometric interaction of protein basic groups with detergent ions. With heat-denatured protein, however, the composition varies continuously through this region. Beyond the ratio of 3 parts of protein to 1 of detergent, an increase in the proportion of detergent still results in combination with the protein until an upper limit is reached, corresponding to a

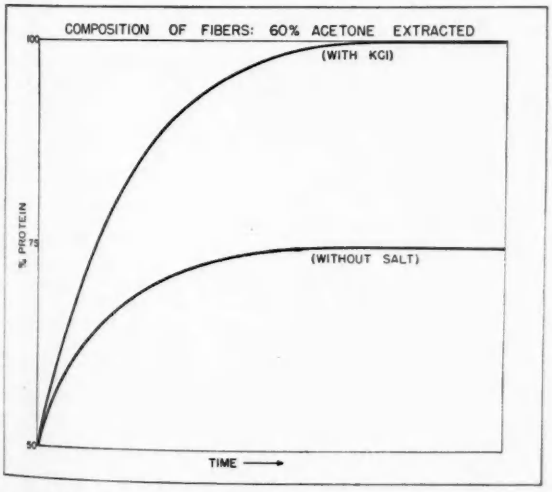



FIG. 12. *Recovery of detergent from 50/50 egg albumin—alkylbenzene sulfonate complex. Using washed fibers and 60 percent acetone, all detergent except the 3-to-1 proportion is removed. With electrolyte present, all detergent is extracted by the acetone.*

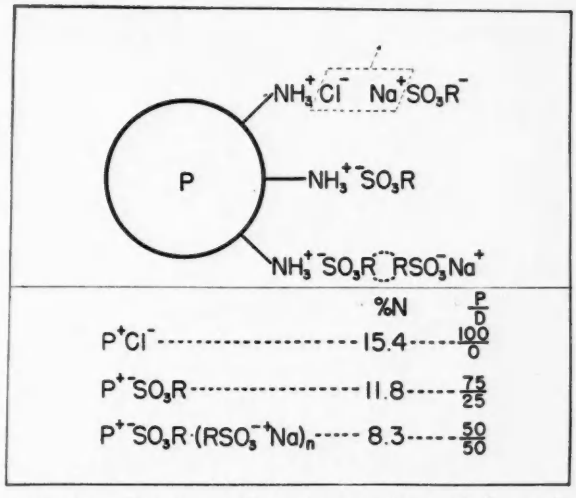



FIG. 13. *Diagrammatic representation of formation of complexes of egg albumin and dodecylbenzene sulfonate. The basic groups of protein unite through ion exchange with the sulfonate to form electrostatic complexes. When all 43 basic groups are saturated, the complex contains the 3-to-1 proportion of protein to detergent. Additional detergent is bound through weak non-polar forces to give 50/50 proportion favorable for fiber formation.*

TABLE III. REGENERATION OF PROTEIN FROM COMBINATION WITH DETERGENT

(Extra bound detergent is removed with 60% acetone after removal of inorganic electrolyte by washing in water. The stoichiometrically bound detergent is removed by 60% aqueous acetone after exchange with inorganic anion.)

Fiber Formation and Regeneration
Egg albumin: Sodium dodecylbenzene sulfonate
(M.W. 45,000) (M.W.$_{(ion)}$ 325)

| Protein-detergent spinning solution→ (19% solids) | | Fiber: Water→ washed | Fiber: →60% acetone→ extracted | Fiber: →60% acetone +KCl extracted |
|---|---|---|---|---|
| % N (dry basis) | | 8.3 | 11.8 | 15.4 |
| Protein / Detergent | Weight ratio | 53 / 47 | 75.6 / 24.4 | 99 / 1 |
| Protein / Detergent | Dry basis | 53 / 47 | 75.6 / 24.4 | 99 / 1 |
| Basic groups Per protein molecule / Detergent ions | | 43 / 123 | 43 / 45 | 43 / 1+ |

ratio of approximately 1 to 3 of protein to detergent, which is about 9 detergent ions for each basic group of the protein.

Similar electrophoretic behavior has been found to occur between native protein and detergent ions in solutions as alkaline as pH 8, and combination between the protein and detergent also occurs in solutions beyond pH 11, as judged by chemical analysis. Normally the protein basic groups would not be ionized in such strongly alkaline solutions, and electrostatic interaction would not be expected to occur, but it is possible that the strong affinity of the protein for detergent ions may shift the equilibrium sufficiently to favor such interaction.

The complexes containing the 3-to-1 proportion, as well as those containing the same proportion together with the additional bound detergent, are readily precipitable by electrolytes. There are, however, important distinctions in the nature of the precipitate from each type. Only those having additional detergent are slimy and exhibit the flow properties commented upon above. The precipitates containing only the 3-to-1 proportion of protein and detergent are flocculent and do not flow together. As the proportion of detergent in the complex is increased above this ratio, the precipitates formed in such solutions by addition of electrolyte become increasingly slimy. When dried precipitates, containing varying proportions of protein to detergent, were subjected to x-ray diffraction analyses, none showed evidence of combination under this condition; the protein and detergent appeared as separate phases, each having its characteristic identity pattern. From this behavior of native protein and detergent and from the fact that both the protein and the detergent micelles had the same sign of electric charge, it was at first thought that the combination in solution involved weak forces between non-polar groups of the protein and of the hydrocarbon residue of the detergent ions [19].

*c. Additional Studies to Confirm Electrostatic Nature of 3-to-1 Combination of Egg Albumin with Alkylbenzene Sulfonates.* (1) Electrophoretic Analyses. Electrophoretic analyses of mixtures of native egg albumin and sodium dodecylbenzene sulfonate indicate no significant changes in the 3-to-1 combining ratio in the region of constant composition when the total concentration is varied eightfold upwards from 0.25 percent solids; these analyses would indicate that a loose association complex is not involved.

Several other well-defined proteins mixed with detergent have been examined electrophoretically in the Western Regional Research Laboratory. Beta-

FIG. 14. *Protein-detergent filaments fused together by heat and pressure in presence of water.*

lactoglobulin and serum albumin * combined with sodium dodecylbenzene sulfonate on the alkaline side of their isoelectric points in a manner similar to that found with native egg albumin. Combination occurs in ratios corresponding to the number of basic groups in these proteins when mixed in solutions containing a high proportion of the native protein. The behavior of crystalline pepsin with detergent is of particular interest, since this protein contains at the most only two or three basic groups per molecule. Slight or no combination was observed at pH 6.5 with sodium dodecylbenzene sulfonate; this observation is consistent with the view that basic groups are essential for combination between the protein and anionic detergent salts.

Electrophoretic examination of mixtures of either native or heat-denatured egg albumin with a non-ionic detergent (a polyether alcohol) showed no evidence of combination in either case; this finding is in agreement with the hypothesis that strong polar groups in the detergent are requisite to interaction with protein, although the absence of long non-polar chains may have been responsible for the failure to combine.

No combination appears to occur between native egg albumin and sodium benzene sulfonate or sodium naphthalene sulfonate, as judged by electrophoretic analyses. With isopropyl naphthalene sulfonate, characteristic interaction occurs, thus indicating that the size of the anion is also important.

(2) Chemical Analyses. The effect of a long-chain hydrocarbon salt on egg albumin in which basic groups had been blocked with phenyl isocyanate has also been examined. When treated with phenyl isocyanate by a method developed by Fraenkel-Conrat and others in the Western Regional Research Laboratory [20], egg albumin is insoluble. After standing in contact with a 5-percent aqueous solution of alkylbenzene sulfonate for two weeks and then being washed with water, the treated egg albumin had the same nitrogen content as before the treatment; thus it appears that no significant combination occurred between the treated protein and the detergent.

TABLE IV. COMPARISON OF DODECYL SULFATE AND DODECYLBENZENE SULFONATE BINDING CAPACITIES OF EGG ALBUMIN

(Experimental values of nitrogen content of fibers washed free of loose bound detergent with 60% acetone are compared with theoretical values of nitrogen content of detergent complexes containing 1 detergent ion for each basic group.)

| Theoretical | % N | Experimental Fibers | % N |
|---|---|---|---|
| | | Water-washed—60% aqueous acetone extracted | |
| | | Egg albumin $(Cl)_{43}$ | 15.6 |
| Egg albumin (dodecyl sulfate)$_{43}$ | 12.4 | Egg albumin dodecyl sulfate | 12.6 |
| Egg albumin (dodecyl-benzene sulfonate) | 11.9 | Egg albumin dodecyl-benzene sulfonate | 11.8 |

The behavior in neutral solution of arginine hydrochloride toward sodium dodecylbenzene sulfonate is similar to that of egg albumin. Formation of a complex occurs and, as with the proteins, the complex precipitates on addition of electrolyte, and its composition, judged from nitrogen analyses, varies in proportion to the amount of detergent used in the mixture. Complexes having as many as 12 detergent ions for each arginine molecule, which would correspond to 3 ions for each nitrogen ion of the arginine, have been prepared. It does not seem probable that the non-polar portion of arginine could attract all of this detergent.

An experiment in which pulverized nylon † was allowed to stand ten days in alkylbenzene sulfonate showed no significant amount of detergent uptake; apparently substituted amide groups do not combine with detergent.

(3) Extraction of Detergent from Complexes. In preliminary studies of a number of solvents, acetone was particularly effective in extracting detergent and especially 60-to-70-percent aqueous acetone. With this solvent, detergent could be extracted, leaving the insoluble protein. It was found that the 60-percent acetone effected practically complete recovery of the detergent from fibers prepared by salt precipitation and drawn by hand. This behavior indicated that all the detergent was bound by relative weak non-polar bonds.

Further experimentation, however, showed that when the last traces of coagulating electrolyte were completely removed from the fibers by washing with

* Putnam and Neurath have reported evidence of stoichiometric combination between serum albumin and long-chain sulfates at a pH alkaline to the protein isoelectric point [*J. Am. Chem. Soc.* **66**, 1992 (1944)]. See also Parkhurst and Smith's discussion of gelatin with dodecylsulfate [*Trans. Faraday. Soc.* **40**, 565 (1944)].

† Supplied through the courtesy of E. I. du Pont de Nemours & Co.

water prior to extraction by aqueous acetone, there was a profound difference in results. In this case only the extra bound detergent was removed, leaving the 3-to-1 combination of protein and detergent.

The results from a typical experiment are summarized in Table III. It is seen that the control fibers washed free of electrolyte maintain the excess detergent corresponding to a ratio of 123 detergent ions to the 43 protein basic groups, essentially the same as the ratio used for spinning. Extraction of these fibers by 60-percent acetone removed only the detergent bound in excess, leaving roughly the same number of detergent ions as basic protein groups. When electrolyte is present during the extraction, as shown in the last column, practically complete recovery of detergent is effected. Results obtained with sodium dodecyl sulfate are compared with those obtained with sodium dodecylbenzene sulfonate in Table IV; as seen in this case, too, the values found experimentally for nitrogen correspond with the values calculated for stoichiometric combination of the detergent ion with the protein basic groups. The reversibility of these reactions is seen in the behavior of fibers from which all of the detergent has been removed. When treated with sodium dodecylbenzene sulfonate in the absence of added inorganic electrolyte, chloride ions are displaced and detergent is bound. Similar exchange behavior is found with other sulfonate ions. For example, if fibers containing no detergent are treated at pH 7 with the dye Orange G (also called Wool Orange 2 G), a naphthalene disulfonate, this dye is taken up. On addition of potassium chloride to the solution, the dye is displaced. In aqueous acetone mixtures the dye is more readily displaced by chloride than in water alone, even though the dye is more soluble in water than in the aqueous acetone mixtures. Orange G is of particular interest for these studies, because this dye has been found by Fraenkel-Conrat [21] to combine stoichiometrically with basic groups of proteins. In this case apparently no additional combination over that bound stoichiometrically occurs in the presence of excess dye, and because of this fact the dye has been found useful for quantitative colorimetric measurement of the number of basic groups in protein. This dye does not behave as if it were highly associated in solution as micelles (or colloidal ions).

When egg-white fibers containing sufficient detergent ions to cover all of the basic groups are treated with Orange G in dilute solution, no dye is taken up. In concentrated aqueous solutions, however, the dye will replace the detergent.

That high-molecular-weight anions are bound to proteins more tightly than are chloride ions is shown by the work of Harris, Steinhardt, and coworkers [17]. We find that when egg albumin chloride combines with sodium alkylbenzene sulfonate, at pH 6.5, a measurable increase in volume of solution occurs. This increase is apparent evidence of change in the distribution of water (i.e., electrostriction), which would result from the tighter binding of the sulfonate anions as compared with the chloride ions.

As stated earlier, the protein-detergent precipitates that had been salted out from mixtures of protein and detergent and then dried showed no evidence of combining when analyzed by x-ray diffraction. When the dry material was prepared with no inorganic electrolyte present and re-examined, a significant increase in the characteristic identity period of the detergent was found. This change in period corresponds with what would be expected if the protein chains lie perpendicularly to, and between, the polar groups in the lamellar form of the detergent. It is apparent that when inorganic anions are present, exchange of these anions with detergent ions takes place as the solutions are concentrated by drying.*

* In the electrophoretic experiments the relatively low concentration of buffer anions was apparently not sufficient to prevent electrostatic combination with detergent anions.

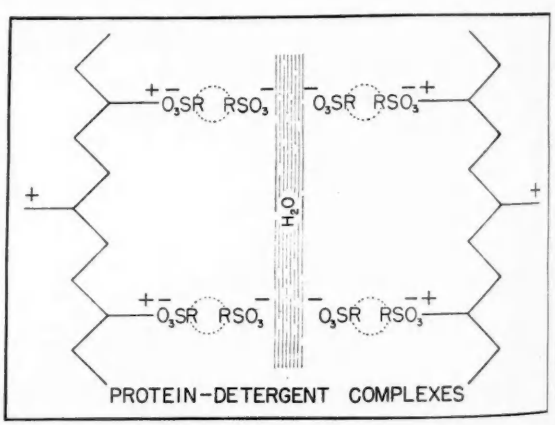



FIG. 15. *Proposed structure of protein-detergent complexes. The extra bound detergent which is attached to that stoichiometrically bound gives rise to a distribution of similarly charged groups along the peptide chain, which repel similarly charged groups of an adjacent chain, thus favoring flow.*

TABLE V. SHAPE RATIO OF EGG ALBUMIN-DODECYLBENZENE SULFONATE COMPLEXES IN DILUTE SOLUTION AS DETERMINED FROM INTRINSIC VISCOSITY MEASUREMENTS

| Egg albumin + | Stoichiometrically bound ions | + Extra bound ions | $\left[\frac{\eta_{sp}}{c\rho}\right]_{(c\rho \to 0)}$ | Ratio: Length/width Elongated | Flattened |
|---|---|---|---|---|---|
| | 43 $Cl^-$ | 0 | 4.6<br>5.5 | 4<br>5 | 5<br>6 |
| | 43 $^-SO_3R$ | 0 | — | — | — |
| | 43 $^-SO_3R$ | 53 $^-SO_3R$ | 3.6 | 3 | 3 |
| | 43 $^-SO_3R$ | 103 $^-SO_3R$ | 3.0 | 2 | 2 |
| | 43 $^-SO_3R$ | 107 $^-SO_3R$ | 2.9 | 2 | 2 |
| | 43 $^-SO_3R$ | 300 $^-SO_3R$ | 3.3 | 2 | 2 |
| Theoretical for sphere | | | 2.5 | 1 | |

Calculated shape

(*a*) as 4 chains $\frac{360}{90} = \frac{4}{1}$

Egg albumin sulfonate$_{43}$ + sulfonate$_x$
10 Å + 2(20)Å + 2(20Å) = 90Å

(*b*) as 1 chain $\frac{1,440}{90} = \frac{16}{1}$

(4) Conclusions Regarding the Nature of Forces Involved in the Combination of Egg Proteins with Long-Chain Hydrocarbon Salts. It is apparent from these experiments that the protein basic groups combine electrostatically by ion exchange with the anions of detergent salts. Additional detergent is bound when the electrostatically bound detergent is present. This extra detergent is presumed to be combined through non-polar attraction to the detergent bound first. These non-polar forces would appear to be the same as those that bind detergent ions into micelles. The extra bound detergent can be removed by the acetone when an additional anion is present for the exchange (Figures 12 and 13).

(5) Flow Properties of Protein-Detergent Complexes. We have already referred to the highly viscous character of protein-detergent mixtures in concentrated solution. Solutions having compositions suitable for spinning exhibit plastic flow, birefringence of flow, and, as previously stated, will yield fibrous precipitates on dehydration by acetone. Also, as stated, such solutions on dilution have a viscosity not appreciably different from that of similar concentrations of native egg albumin in solution by itself; this fact suggests an asymmetry of the kinetic units similar to that observed for the native corpuscular protein.

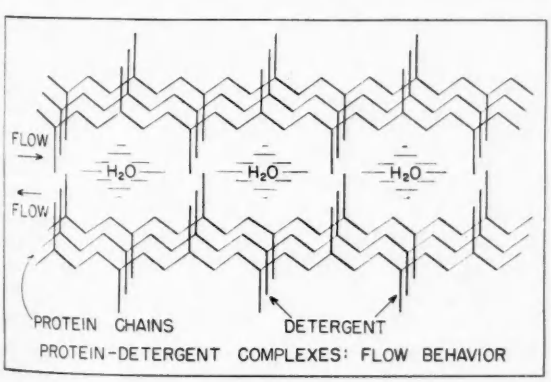



FIG. 16. *Amplification of structure shown in Figure 15 to account for simultaneous flow of several peptide chains.*

Measurements of the intrinsic viscosities of dilute solutions of mixtures of crystalline egg albumin and sodium dodecylbenzene sulfonate in various proportions are summarized in Table V. Values representing two possible shapes are shown; one is calculated on the assumption that the particles are ellipsoidal and the other on the assumption that they are platelets. From either calculation it appears that the particles of protein combined with varying proportions of detergent in the dilute solution are not significantly asymmetrical and are similar to values of 4 to 1 obtained from measurements on the pure native egg albumin.

If we take into account the added width, contributed by the detergent ions along both sides of the unfolded peptide chain, it is possible to reconcile the symmetry of the complexes in dilute solutions with the concept of an unfolded albumin molecule having a four-chain structure. The length of these chains, it will be recalled, is about 350–360 Å. and the axis ratio in the extended state is about 36 to 1. If such a chain is considered to have a double layer of dodecylbenzene sulfonate ions on each side (with length of each ion assumed to be extended to 20 Å.),

then the new asymmetry value would be roughly 36 to 9 or about 4 to 1. This value is in approximate agreement with the values found experimentally. On the other hand, if the egg albumin molecule is considered to be a single chain about 1,400 Å. in extended length, then to account for viscosity behavior in dilute solutions it would be necessary to assume folding of the complexes. From these considerations the behavior of concentrated solutions which exhibit plastic flow can be explained either by assuming linear association of the less asymmetric units, or, if egg albumin is a single long chain, by assuming unfolding similar to the behavior that appears to take place in various proteins in high concentration in the absence of electrolyte.

In sufficiently high concentration, solutions of protein and detergent may set to gels that exhibit strain birefringence. Gels have been made with egg albumin and sodium dodecyl sulfate which, if pulled suddenly, will tear; but if the strain is applied slowly, they will flow. Fibers can be made by flowing such material to the desired shape and then allowing it to set. After removal of some of the water, these fibers can then be cold-drawn to give high birefringence.

It is of interest to consider the forces that may be responsible for the association of protein-detergent units and for the structural properties observed. Attraction might occur between detergent residues or between protein groups of adjacent chains. Offhand, it might be expected that the presence of detergent ions along the protein chain would inhibit interaction between protein groups. That inhibition does occur is seen in the fact that 2-percent gelatin solutions, which ordinarily gel on standing, will not gel when more than 1 percent of dodecyl sulfate is present. Such solutions become highly viscous but the viscosity is lowered by the addition of urea, a good dispersing agent for protein. This behavior indicates that the observed interaction might involve hydrogen bonding between protein groups. Further confirmation of this interpretation is seen in the behavior of mixtures of ovomucin with detergent. This protein forms gels in the presence of or in the absence of detergent; in either case the gels are liquefied by reducing agents. Still further evidence for protein group interaction is seen in the character of the protein fibers which contain detergent. Egg albumin fibers that contain the electrostatically bound detergent can be oriented; such fibers have a tenacity value comparable with that of stretched and completely regenerated fibers. Interaction between hydrocarbon residues

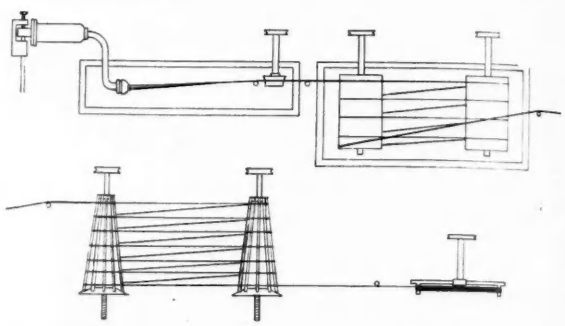


FIG. 17. *Diagrammatic representation of the mechanical spinning of protein-detergent complexes. The salt-coagulated filaments are led over drums through water to remove electrolyte, over cones for stretching during drying, and then are wound into skeins on reels.*

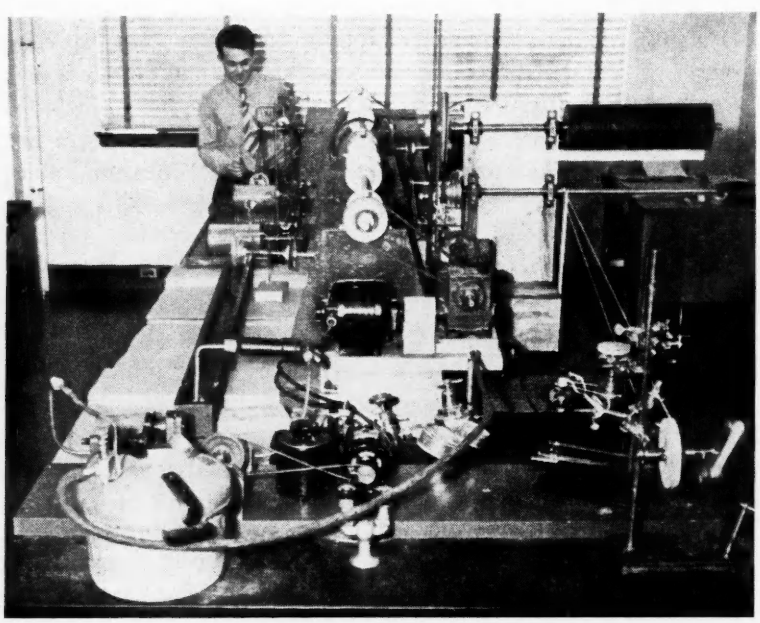


FIG. 19. *The experimental spinning equipment, with the exception of the steam chamber, is on a flat desk-top. Air pressure forces protein-detergent complex from pressure pot to pump, which feeds the material at constant rate to the spinneret through a candle filter. Power for most moving parts is derived from a main shaft through V-belts using variable-pitch pulleys.*

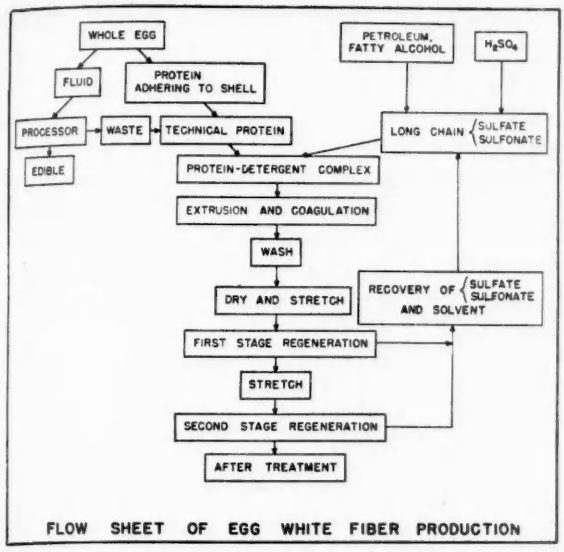



FIG. 18. *Steps in preparation of regenerated fibers from technical egg white.*

from such short chains would not be expected to give strong fibers.

The flow behavior of protein-detergent complexes is determined ultimately by the presence of water. When completely dry, the complexes are brittle. The effect of heat and pressure in causing protein-detergent fibers containing some water to fuse is shown in Figure 14. When much water is present and stress is applied to the fibers, the resulting flow appears to be merely a slippage along planes, and the fibers become thinner with no increase in tenacity. If the water content is reduced, interaction between protein chains can occur, and the stretch applied causes increase in tenacity. When equilibrated in an atmosphere of 90 to 95 percent relative humidity, undrawn fibers containing excess bound detergent can be drawn cold to fibers that are fair in strength and highly birefringent. These are as highly oriented and as strong as those that have been prepared from partially extracted fibers drawn in steam. When exposed to an atmosphere of steam or hot water, fibers containing electrostatically bound as well as extra bound detergent swell and disintegrate, but if the extra bound detergent is first removed by extraction with aqueous acetone, the fibers can then be readily drawn in steam to a high degree of molecular orientation with good tenacity. Upon removal of the electrostatically bound detergent, the fibers become more pliable and elastic. The presence of the electrostatically bound detergent is advantageous in the drawing in steam. Fibers that have been completely extracted can be drawn in steam, though not so easily. Even though stretching in steam enables the fibers to be stretched and thus oriented, this procedure, too, is not yet sufficiently developed to be considered practical on a large scale. Various aspects of stretching in the cold and in steam are under investigation.

The foregoing aspects can be summarized by reference to a structural model shown in Figure 15. This model shows the detergent bound electrostatically to the basic groups along the peptide chain and also the extra bound detergent, which presumably combines with the residues of detergent bound electrostatically. When the extra bound detergent is present, there is a layer of similarly charged ions distributed along the protein chain. These groups, ionized in water, will

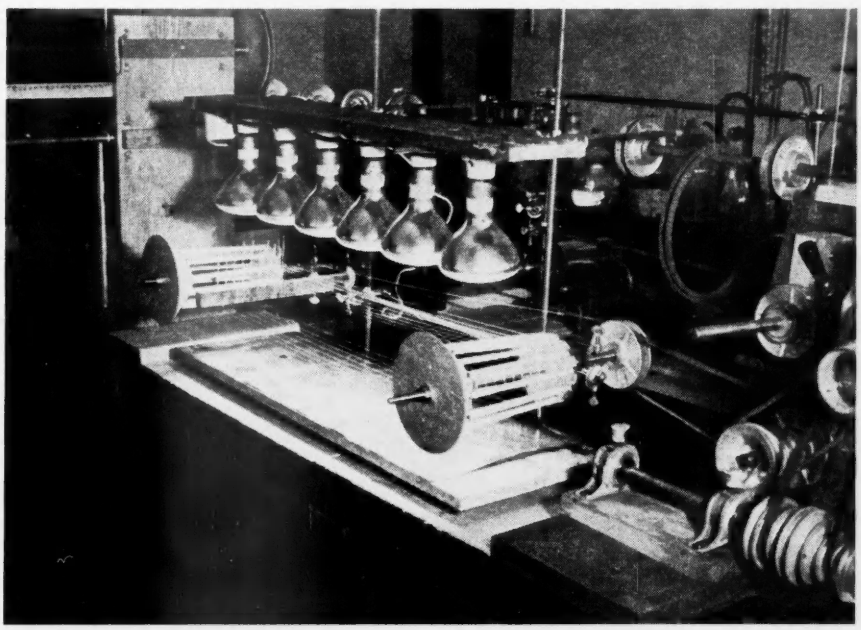


FIG. 20. *As the filaments are dried by infra-red light they are stretched by passage over variable-pitch cones.*

repel similarly charged groups on adjacent chains. It is assumed that when stress is applied, flow will occur across this plane. When the protein chains are sufficiently close together in concentrated solution, interaction between them can occur and the groups of chains may flow together (Figure 16).

According to this structure the complex containing only the electrostatically bound detergent would be expected to be more hydrophobic than either the protein alone or the protein containing excess bound detergent. Tests with and without detergent present have shown that the equilibrium water content of the first-named complex was 70 to 80 percent of that of the protein alone and of the protein with extra bound detergent.

## Fiber Spinning

### *1. Mechanical Apparatus*

There are several ways in which fibers can be made from protein-detergent complexes. Some of these have already been mentioned. Fibers can be made by precipitation, with electrolyte, of the complexes containing extra bound detergent followed by drawing (or possibly extrusion). They can be prepared from concentrated protein-detergent complexes by dehydration with acetone, and can be made also by flowing of viscous solution followed by dehydration by exposure to circulating air.

Probably the most practical method for preparing uniform filaments on a large scale is by wet spinning in a manner similar to that employed in making viscose rayon. A diagram of the mechanical arrangement used in the Western Regional Research Laboratory for the study of spinning of protein-detergent complexes is shown in Figure 17. Only conventional pumps, filters, and spinnerets are used. Figure 18 shows the general scheme followed in the experimental process with technical egg white. After coagulation by salt the filaments are led over drums and through water baths to remove the electrolyte. They are then dried over cones whose pitch can be varied for the application of controlled stretch. The fibers are then wound on bobbins or reels. At present, and for the experimental studies, the extra bound detergent is next removed from the fibers with several changes of 60-to-70-percent aqueous acetone at room temperature. Next the fibers are stretched by differential speeds of reeling through a steam tunnel. Finally, the electrostatically bound detergent is recovered with 60-percent acetone containing electrolyte and the fibers are ready for further treatment. No hardening agents are used during the spinning-and-stretching operation.

Pictures of the assembly and various parts are shown in Figures 19 and 20. All of the equipment is on a flat desk-top. Power for the various units is taken from a main drive with variable-pitch pulleys for speed regulation.

### *2. Fibers from Egg-White and Chicken-Feather Proteins*

Most of the work in the Western Regional Research Laboratory with the mechanical process has been confined to technical egg white and chicken-feather keratin. Dispersions of the proteins having desirable spinning properties have been made in technical sodium alkylbenzene sulfonate and sodium dodecyl sulfate. For best results it is well to use a viscosity of 100 to 150 poises, a composition of 60 to 40 parts by weight of protein with 40 to 60 parts of detergent, and a total concentration of about 19 to 21 percent of solids. With fresh, so-called unfermented egg white, solutions of this composition may have viscosities greater than 150 poises and may form gels. This effect may be due to the presence of ovomucin, for, by the addition of as little as 0.1 percent of monothioglycol or a similar reducing agent, the viscosity can be lowered in a manner similar to that known to occur when solutions of ovomucin are treated similarly.

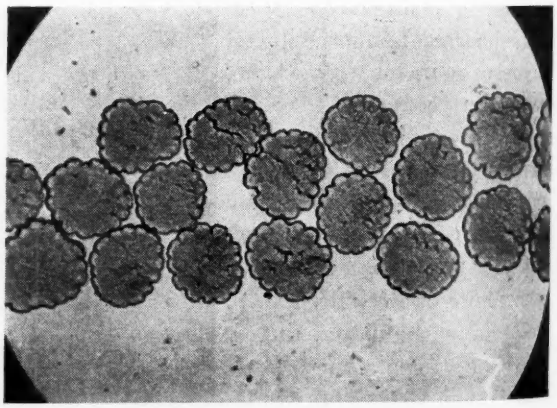


FIG. 21. *Microscopic cross-section photographs of fused multifilament fibers made from egg white. All filaments issuing from 25-hole spinneret are fused into a single thread.*

*(Cross-section photographs made by courtesy of Dr. T. L. W. Bailey, Jr., of the Southern Regional Research Laboratory.)*

*a. Preparation of Spinning Solutions from Egg-White Solids.* Dried egg white as obtained from the processor is dissolved in water to make a solution of 25 to 30 percent and the solution is clarified by filtering or centrifuging. (A fine suspension of nondispersed fat or globulins will dissolve when the detergent is present.) Similarly, a solution is prepared which contains 25 to 30 percent of Nacconol NRSF.*

A good spinning "dope" contains between 60 parts by weight of protein and 40 of Nacconol and 40 of protein and 60 of Nacconol with the dope containing 18 to 24 percent of solid material. The best results are obtained with a slight excess of Nacconol and a viscosity of 70 poises or over.

The "dope" is prepared by adding to the Nacconol solution the calculated amount of water and 0.1 percent of mercaptoethanol, which greatly hinders gelation. The egg solution is then poured in with rapid stirring and the viscosity immediately rises. After it is mixed well the "dope" is aged overnight in a vacuum desiccator (to deaerate it) and there is a further, though not large, rise in viscosity. It is now ready to spin.

The presence of considerable yolk does not seem to interfere with the spinning or to alter the properties of the finished fibers. Most of the fat is removed by the acetone. Evidence of spoilage does not materially affect the quality of the fibers. As a matter of fact, older, fermented egg white has proved better for spinning than strictly fresh material.

Stretched and regenerated fibers made from egg-white protein by hand drawing of the salt-precipitated complexes are in general as good in quality as those made from crystallized egg albumin. Fibers showing a high degree of orientation and desirable mechanical properties have been obtained. In this manner fibers showing similar properties have been prepared for comparative studies from a variety of corpuscular and fibrous proteins, including native and heat-denatured egg albumin, blood fibrinogen, hog thyroglobulin, soybean protein, casein, dispersed wool, and horn, hoof, and chicken-feather keratins. The preparation of fibers with anionic detergents is, of course, necessarily limited to proteins having sufficient number and distribution of basic groups, although the proteins having carboxyl groups appear to be capable of similar manipulation by cationic detergents.

*b. Preparation of Spinning Solutions from Chicken Feathers.* Methods for making dispersions of chicken-feather keratin have been described by C. B. Jones, formerly of this Laboratory, and D. K. Mecham [22]. Feathers can be dispersed in alkaline sulfide solutions. As with many proteins, the precipitates from such dispersions do not have desirable flow for spinning. But with the addition of sodium alkylbenzene sulfonate or alkyl sulfate to the alkaline solution in similar proportion to that used with the egg-white protein, the precipitates formed show desirable flow properties. In recent studies, feather keratin was found to be readily dispersed at pH 6.5 in long-chain sulfonates or sulfates and yielded good spinning solutions and desirable fibers. Preparation of such a dispersion with sodium bisulfite as a reducing agent is as follows:

Adjust a 10 percent Nacconol NRSF solution containing 1 percent $NaHSO_3$ to pH 6.5 and then heat to boiling. To the boiling solution add 1.6 parts of washed and dried chicken-body feathers for each part of Nacconol NRSF, and boil slowly for one-half hour with occasional stirring. Dilute with a volume of boiling water equal to one-half the volume of the

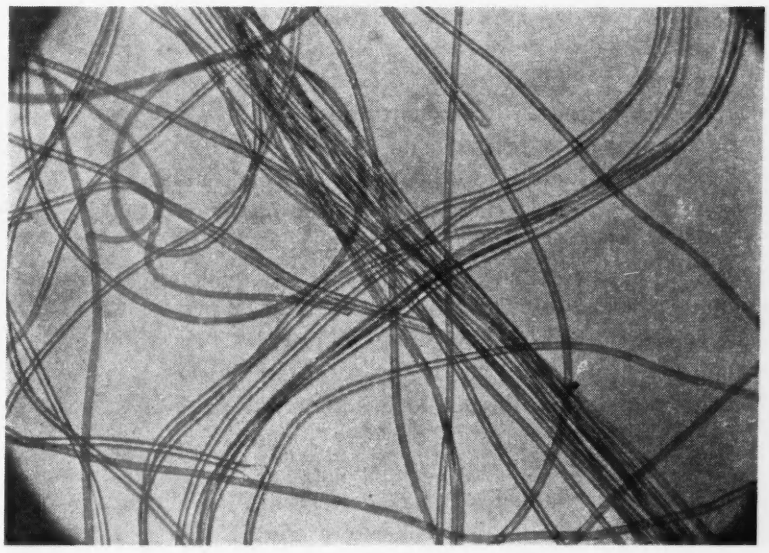


FIG. 22. *Mechanically spun single-filament egg-white fibers (magnification 150 ×).*

*A commercial alkylbenzene sulfonate supplied by the National Aniline Division of Allied Chemical and Dye Corporation.

TABLE VI. TABULATION OF PROPERTIES OF EGG WHITE FIBERS (FROM FRESH EGG WHITE—LYSOZYME EXTRACTED) FROM A SINGLE EXPERIMENT

| | | |
|---|---|---|
| Spinning dope | | |
| 486 cc. 24.6% alkylbenzene sulfonate (Nacconol NRSF) | | |
| 448 cc. 20.6% egg-white protein | | 45 protein |
| 88 cc. water | | 55 detergent |
| 1 cc. monothioglycol | | |
| Coagulating bath | | |
| Saturated magnesium sulfate | | |
| Formic acid pH 2.6 | | |
| (100-hole spinneret—fibers fused) | | |
| Extraction and stretch | | |
| 60% aqueous acetone—5 days (5 changes) | | |
| Stretched 200% in steam | | |
| Properties of Regenerated and Stretched Fibers | | |
| | Dry | Wet |
| Diameter | 80 microns | 85 microns |
| Tenacity | | |
| (lbs./sq.in.) | 19,300 | 6,900 (−64% dry) |
| (g./den.) | 1.16 | 0.41 |
| Total elongation at break | 15% | 24% |
| Tension to stretch 1% | 0.52 g./den. (reversible to 3% stretch) | 0.12 g./den. (irreversible) |
| Density | 1.28 | — |
| Birefringence | Positive +0.008 | |
| Orientation | Good beta | — |

original Nacconol solution and continue boiling for another half-hour. Stir occasionally. Filter the hot solution through a glass cloth into a large filter flask with gentle vacuum. Extract the undissolved residue four times, using in all a volume of boiling water equal to about three-fourths the volume of the original Nacconol solution. Filter through a fast paper, using Filter Cel. Then evaporate the dispersion to dryness in trays, at room temperature, with a current of air blowing over the trays. Complete the drying in a vacuum desiccator over $P_2O_5$ and ball-mill the bone-dry complex for a short time. Following analysis for nitrogen, a factor of 6.21 is used to calculate the protein-Nacconol ratio.

Because a good spinning "dope" contains about 45 parts of feather keratin to 55 parts of Nacconol and because the powdered complex is a little higher in protein, a small calculated amount of Nacconol is added to the necessary amount of water and enough complex is added to make a dope containing 22 percent solids, of which 45 percent is protein. This complex is heated with stirring in a 60°C bath for about 40 minutes and the hot dope is filtered through a glass cloth with very gentle suction. After ageing overnight, the dope is ready to be spun.

*c. Coagulating Baths for Protein-Detergent Fibers.* For precipitation of the mechanically extruded protein-detergent complexes, a saturated solution of magnesium sulfate, adjusted to pH 1 to 2 with sulfuric acid, is effective. The precipitation is determined by cations and follows the order predicted by the Schulze-Hardy rule. With the exception of magnesium, the higher-valence cations (aluminum, barium, and calcium) give flocculent precipitates even with the extra bound detergent present. Precipitates formed by sodium, ammonium, and magnesium ions have characteristic flow properties. (When precipitated by cations at neutral or alkaline pH and then washed with water, the fibers may swell and dissolve.)

A significant aspect of the precipitation by electrolytes is the fact that flow is evident for a short period, after which the precipitate toughens and can no longer be drawn. If the precipitate is washed with water, it will remain soft. It would seem that the hardening is the result of anion exchange, resulting in displacement of the detergent ions from the protein.

The character of the precipitate varies with the ratio of protein to detergent. In general, we have adopted weight ratios of protein to detergent that vary from 60/40 to 40/60. These ratios would correspond, in the case of egg albumin, to ratios of about 2 to 4 detergent ions per protein basic group. The higher the proportion of detergent, the greater is the tendency of the precipitated filaments to cohere; and filaments that fuse together remain so even after removal of detergent (Figure 21). With a higher proportion of protein, the filaments remain separate (Figure 22). In this regard, no significant difference in the behavior is observed between alkyl sulfates and alkylbenzene sulfonates. With feather

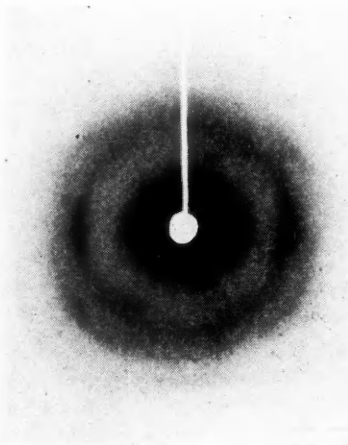


FIG. 23. *X-ray photograph (by Dr. Palmer) of oriented egg-albumin fiber showing β-keratin structure.*

keratin, the precipitated fibers are not washed in water prior to extraction with acetone.

### Properties of Stretched and Extracted Fibers

Stretched and regenerated fibers prepared from egg albumin and technical egg white and also from chicken-feather keratin by this method have shown a high degree of orientation [23, 24] with distances corresponding to those of $\beta$-keratin of stretched fibrous proteins (Figure 23).

Along with the increase in orientation of the fibers there is corresponding increase in tensile strength. In some instances tenacity values for egg-white and chicken-feather fibers of greater than 3 grams per denier have been obtained under standard conditions of humidity and temperature. When wet the unhardened fibers lose 60 percent or more of their strength. Mechanically spun and regenerated filaments are elongated 2 to 20 percent at break, depending upon the orientation, but when detergent is present the elongation is consistently low.

Table VI summarized results of an experiment with fresh egg white. Various properties of the uncured fibers are compared, wet and dry.

In order to overcome low wet strength (a characteristic of all synthetic protein fibers) experiments are being conducted to establish primary valence cross-linkage between the parallel protein chains. A discussion of the properties of these fibers, together with results of chemical and physical treatments, will be presented in later communications.

### Summary and Conclusions

In this discussion the use of hydrocarbon salts in the preparation of spinning dispersions from corpuscular as well as fibrous proteins has been described. Egg white and chicken-feather keratin have been used as typical proteins. By appropriate stretching along with the removal of detergent, highly oriented fibers having the $\beta$-keratin structure typical of natural protein fibers have been made.

With crystalline egg albumin as a model protein, it has been shown that primary interaction between proteins and long-chain hydrocarbon salts is electrostatic, involving the basic groups of the protein when anionic detergents are used. Additional detergent can be bound, presumably by the residues of the detergent bound electrostatically and by non-polar forces. When additional detergent is bound, the complex acquires flow properties that are necessary in the fiber-making process.*

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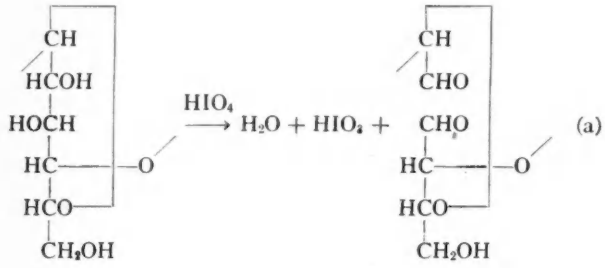
# Cellulose Studies

## I. Reaction of Oxycellulose with Aqueous Acids and Alkalies

**Eugene Pacsu**

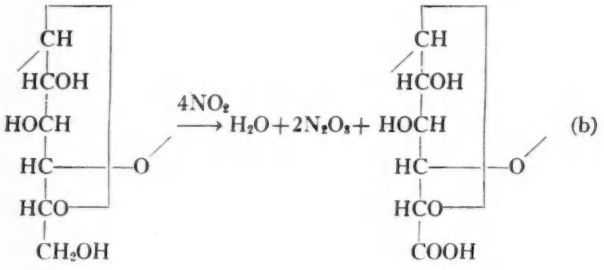
*Contribution from the Textile Foundation and the Frick Chemical Laboratory at Princeton University*

ALTHOUGH most "oxycelluloses" represent mixtures of products of varying degrees of oxidation, cellulose oxidized by periodic acid (I) [1], and cellulose oxidized by nitrogen dioxide (II) [2], appear to possess structures approximating those demanded by the ideal reactions (a) and (b).




(a)

(I)




(b)

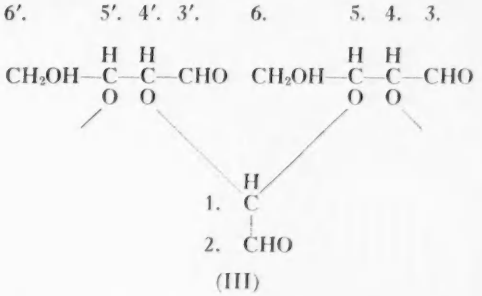
(II)

Since in the various commercial processes the partial formation of oxidized cellulose by a great variety of agents mostly represents an undesirable feature, it is of great importance clearly to understand the properties and chemical reactions of such oxycelluloses as can be regarded to be definite chemical entities. Once the nature and the mechanism of the complicated reactions displayed by such oxycelluloses toward different chemical agents, particularly alkali and acid, are fully known, it should be possible to apply this knowledge to the interpretation of the chemical reactivity of the more or less severely oxidized celluloses.

Part of the research program initiated at the Textile Foundation centers around these problems. In the present preliminary paper a few observations are reported which may prove to be significant in the interpretation of the chemical behavior of oxidized celluloses. Also presented in this paper is a working hypothesis which is concerned with the mechanism of the degradation of periodate oxidized cellulose in alkaline medium.

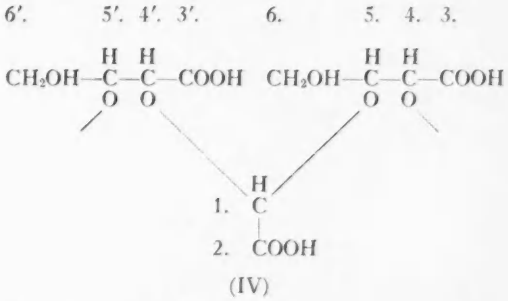
Unruh and Kenyon's [*2b*] results indicate that the nitrogen dioxide selectively attacks the primary hydroxyl groups of the cellulose to yield oxidized materials containing essentially combined uronic acid units ("acidic" type of oxycellulose). In contrast to nitrogen dioxide, periodic acid preferentially oxidizes the two secondary hydroxyl groups of the glucose residues, thus breaking the carbon chain between carbon atoms 2 and 3 and producing two aldehyde groups ("reducing" type of oxycellulose). It is known from Davidson's [3] careful work that reaction (a) is inadequate for the complete representation of the action of periodic acid on cellulose. This author reported that 8.9 percent loss of weight occurred instead of the calculated value of 1.2 percent when apparently one atom of oxygen was consumed by every glucose anhydride unit. He found also that under such conditions formaldehyde (one mole for every 29 units), formic acid (one mole for every 13 units) and carbon dioxide (one mole for every 10 units) were also formed as products of the oxidation reaction. However, the loss of weight (1.5 percent) and the yields of formaldehyde (1:125), formic acid (1:58), and carbon dioxide (1:42) were considerably smaller when sodium metaperiodate instead of periodic acid was used for the same degree of oxidation. As a rule, our oxycellulose was prepared by oxidation at room temperature of surgical cotton (Johnson and Johnson) with about 1*N* sodium metaperiodate solution, the oxygen consumption being one atom as required by the ideal reaction (a). Since the loss of weight was about 1.5 percent under such conditions, the product can

be regarded as possessing essentially the structure expressed by formula (I). The oxycellulose was soluble in hot water, except for an insignificant quantity of swollen particles which were easily removed by the centrifuge. In order to avoid discoloration of the solution, carbon dioxide gas was passed through the aqueous suspension during the four to five hours which were necessary for solution of the oxycellulose on the boiling water bath. The clear, aqueous solution was only feebly acidic to litmus, thus indicating the practically complete absence of carboxyl groups in the oxycellulose. Evaporation of the aqueous solution under diminished pressure resulted in a colorless, brittle material, which again required heating for several hours on the steam bath for complete solution. It was shown by Jackson and Hudson [1] that the hydrolysis of periodic acid oxycellulose by 0.1*N* aqueous hydrochloric acid at 98-99°C for sixteen hours produced glyoxal and *D*-erythrose. The smallness of the yields of the isolated derivatives of these compounds, 20 percent of glyoxalbenzylphenylosazone and 15 percent of brucine *D*-erythronate, was regarded by these authors as due, at least in part, to some destruction of the material during hydrolysis, and to incomplete degradation of the polymer. Michell and Purves [4] suggested that a recombination of glyoxal and erythrose under the influence of the aqueous acid would explain the surprisingly low yields isolated from the hydrolysis of oxystarch and oxycellulose. However, it seems to us unlikely that the experimental conditions of the acid-catalyzed hydrolysis could favor such a recombination to any appreciable extent. A partial destruction of the erythrose set free during the hydrolysis of the oxycellulose appears to be more probable, in view of an early observation by Ellett and Tollens [5], who claimed that *L*-erythrose, on heating with hydrochloric acid, gave rise to lactic acid. In one of our experiments oxidation of periodate oxycellulose with bromine in the presence of sodium bicarbonate, followed by hydrolysis at 100°C of the product in 1*N* hydrochloric acid for five hours, resulted in a 75 percent yield of pure glyoxylic acid 2,4-dinitrophenylhydrazone. The incomplete hydrolysis of the oxycellulose mentioned by Jackson and Hudson is another valid reason why the theoretical yields of the scission products cannot be reached. The comparatively great resistance to acid of the C—O—C linkages is, indeed, one of the most remarkable features of the aldehyde type of oxycellulose. It deserves special consideration in view of the widespread belief concerning the harmful effect of acids on oxidized cellulose. In one of our experiments an aqueous solution of oxycellulose was changed into a 2*N* acidic solution by addition of hydrochloric acid. Evaporation of the solution in an open dish at room temperature caused no apparent change in the properties of the brittle residue; it took several hours' heating on the steam bath to redissolve the material in water after it had passed through the swelling usually shown by untreated oxycellulose. The considerable resistance to acid of the C—O—C linkages in the aldehyde type of oxycellulose is all the more noteworthy since the substance belongs to the acetal type of compounds, which are known to be susceptible to acid-catalyzed hydrolysis. Periodate oxycellulose contains glyoxal half-acetal residues (III),




(III)

in which two erythrose molecules each contribute one secondary alcohol group. Similarly, the carboxylic acid derivative of the periodate oxycellulose should be regarded as consisting of glyoxylic acid acetal residues (IV),




(IV)

in which the alcohol components correspond to two secondary alcohol groups, each belonging to one molecule of *D*-erythronic acid or its γ-lactone.

Thus it is seen that the problem of the chemistry of periodate oxycellulose is shifted to that of the polysemiacetals of glyoxal and the polyacetals of glyoxylic acid. At present, little is known of even

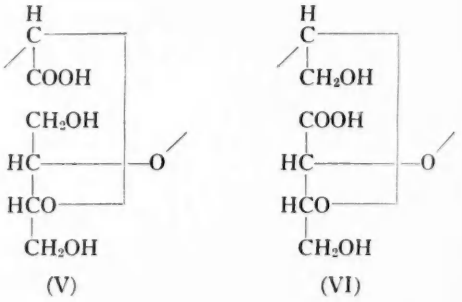
the simplest representatives of these acetals. Harries [6] prepared glyoxal diethylsemiacetal, OHC—CH $(OC_2H_5)_2$, by treatment with ozone of acrolein diethylacetal, $CH_2{=}CH.CH(OC_2H_5)_2$, but did not report its chemical behavior except to state that the compound decomposed at 80° to 90°C into alcohol and glyoxal. Likewise, there are only a very few reports in the literature on the chemical properties of the acetals, such as the dimethyl [7], diethyl [8], and diisobutyl acetals [9], of glyoxylic acid, HOOC—$CH(OR)_2$.

However, these "dialkoxyacetic acids" appear to be more stable toward hydrogen ions than the semiacetal of glyoxal. A thorough study of this type of compounds should yield valuable information, which could judiciously be applied to explain the behavior of the aldehyde type of oxycellulose in acid medium. It is, perhaps, still more urgent to investigate the immediate effect of acids on the scission products of oxycellulose, such as glyoxal, glyoxylic acid, and especially erythrose and erythronic acid. In comparison to the vast amount of information available for the commonly known carbohydrates, the tetroses and their derivatives are still relatively rare or unknown compounds. Their structures and chemical behavior do not follow directly from analogous reactions, which are well understood in the pentose or hexose series.

While the chemical behavior of periodate oxycellulose in acidic medium requires further study, the enhanced reactivity of this type of oxycellulose in alkaline medium presents far more difficult problems. In dealing with a substance which represents a chemical combination between a potential polyhydroxyaldehyde and glyoxal, one is confronted with the numerous reversible and irreversible changes which may take place in the presence of hydroxyl ions. The outstanding feature of such a combination has perhaps not yet been generally appreciated; this refers to the acidic character toward hydroxyl ions of the aldehyde type of oxycellulose. Although an aqueous solution of periodate oxycellulose, as was stated above, is only feebly acidic to litmus, it uses up a considerable quantity of standard alkali solution in the presence of phenolphthalein. However, the end-point of the reaction is usually indefinite [10] and, because of discoloration, which is particularly severe in somewhat more concentrated solutions, it is generally impossible to rely on it with any degree of accuracy. Therefore, methods of determination of the *supposed* carboxyl content of the aldehyde type of oxycellulose by direct or indirect use of alkali must be regarded as fundamentally unsound. Addition of an excess of calcium acetate solution (Lüdtke's method) to the aqueous solution or suspension of the aldehyde type of oxycellulose does not liberate a supposedly equivalent quantity of acetic acid; the apparent consumption of alkali occurs just the same in the absence of calcium acetate. Determination of acidity by direct or indirect use of alkali does not seem to be applicable [2*b*] even to a pure acidic type of oxycellulose, like the nitrogen dioxide oxidized cellulose (II).

In seeking for an explanation of the acidic nature of the periodate oxycellulose in alkaline solution, one should consider the possible transformations which may conceivably take place in oxycellulose molecules of the aldehyde type. Among the transformations, close attention should be given particularly to the anionotropic and the prototropic changes.

An anionotropic change involving the transfer of a $H^-$ (hydride ion) from one aldehyde group to the other within one dialdehyde unit of the chain (Cannizzaro reaction) would give rise to two different derivatives (V and VI)

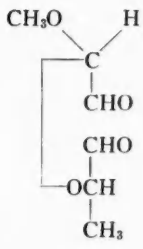



(V) (VI)

of the original dialdehyde unit. Formula (V) corresponds to the erythritol acetal of glyoxylic acid, and formula (VI) represents the *D*-erythronic acid acetal of glycolaldehyde. Since the two reactions may take place at approximately equal rates, the product would probably show a random distribution of both types of units in the chain. It is important to note that this anionotropic transformation requires one equivalent of sodium hydroxide.

It was shown by Fry, Wilson, and Hudson [11] that *L'*-methoxy-*L*-methyl diglycolic aldehyde (VII), obtained by oxidation of α-methyl-*L*-rhamnopyranoside, underwent a Cannizzaro-type reaction when solution of the substance in *excess* alkali was heated

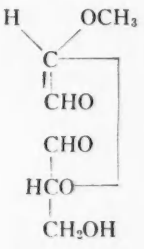
for 5 minutes on the steam bath. During the reaction exactly one mole of alkali was consumed.



(VII)

In our experiment considerable darkening of the solution occurred after the addition at room temperature of *one equivalent* of 1*N* sodium hydroxide solution to the periodate oxycellulose, which was used either in the solid form or in cold aqueous (0.1*N*) solution. After one hour's standing at room temperature the solution was mixed with one equivalent of 1*N* hydrochloric acid. During the addition of the acid the solution lost its dark color and became slightly yellow. The strong acidic reaction of the solution clearly indicated that under the influence of one mole of alkali the originally almost neutral oxycellulose gave rise to acidic products. Addition of brucine to the acidic solution resulted in a mixture of several crystalline and amorphous brucine salts. Although the separation and identification of these salts have not yet been accomplished, preliminary results would seem to indicate that the crystalline products represent the brucine salts of organic acids with low molecular weights. This remarkable result, although preliminary in nature, led us to believe that considerable degradation of the large polymer must have occurred during the reaction with alkali. In connection with this conclusion it should be noted that Fry, Wilson, and Hudson always hydrolyzed the primary product of their Cannizzaro type of reaction by warming the *acidified* solution on the steam bath. The scission products—glycolic aldehyde, glyoxylic acid, propylene glycol, and lactic acid—were then isolated from the acid hydrolysate in the form of suitable derivatives.

In order to ascertain whether or not such an acid-catalyzed hydrolysis is necessary for the breaking up of the primary products, we carried out a Cannizzaro type of reaction on the dialdehyde (VIII) which was obtained by periodate oxidation of α-methyl-*D*-glucopyranoside. However, we used only one equivalent of 0.1*N* barium hydroxide solution instead of an excess of sodium hydroxide solution. After the addition of slightly less than the necessary one equivalent of 1*N* sulfuric acid, and *without* subsequent hydrolysis by acid, the solution was concentrated under diminished pressure. Of the products of the reaction the crystalline semicarbazone and 2,4-dinitrophenylhydrazone of glyoxylic acid were isolated in small yields, 22.5 percent and 22.3 percent, respectively. From this result we have concluded that (1) a weak base like 0.1*N* barium hydroxide solution is sufficient to cause an anionotropic transformation of certain dialdehyde types of semiacetal derivatives of



(VIII)

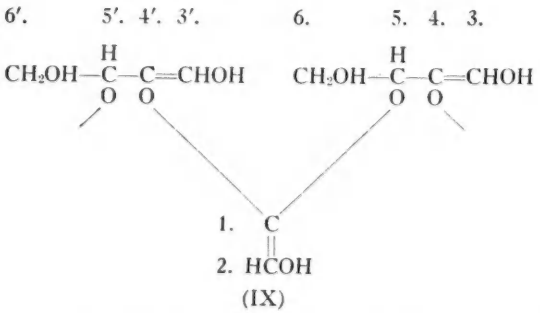
glyoxal; (2) the low yields of the scission products suggest that the hydroxyl ions might initiate reactions other than the Cannizzaro type of transformation; (3) in order to obtain the scission products, hydrolysis by mineral acid of the primary products is not necessary.

In view of the surprisingly great acid-resistance of periodate oxycellulose, the third conclusion above should apply to the primary product of a dialdehyde type of acetal of low molecular weight only. In such products (VII and VIII) the hydrogen ions necessary for hydrolysis may originate from the molecules themselves, which represent strong monobasic acids. On the other hand, the hydrogen ions supplied by the primary products of the periodate oxycellulose (V, VI) certainly ought to be insufficient to cause any considerable damage to the long-chain polymer, since the original periodate oxycellulose (I) can withstand, as was pointed out above, the effect of 2*N* hydrochloric acid. From these considerations it is clear that the validity of our second conclusion should be examined. At this point it should be emphasized that a proposed reaction other than the Cannizzaro type of transformation must account for the apparently complete degradation of the periodate oxycellulose in alkaline medium. In other words, one must explain one of the most puzzling problems

of cellulose chemistry—namely, the obviously easy cleavage by alkali of the C—O—C linkages of the aldehyde type of oxycellulose. In connection with this problem, in the following discussion we shall advance a working hypothesis, which is based partly on known facts and partly on our above-mentioned experimental results. Our hypothesis is offered as a tentative suggestion for the explanation of the nature and mechanism of the reaction between oxycellulose and alkali, and of the mechanism involved in the ageing of alkali cellulose.

On the basis of the electron concept of valence, the mechanism of an alkaline hydrolysis, which is carried out under normal conditions, requires the presence of a carbonyl group to which certain groups, such as OR, $NR_2$ or Cl, are attached. In other words, only the esters, lactones, amides, and halides of the carboxylic acids can be hydrolyzed by alkali, and not the acetals or orthoesters, where the carbonyl group is missing. Indeed, the stability in alkali of the two latter groups of compounds is one of the characteristic properties of these substances. The evident cleavage in alkaline solution of the C—O—C linkages of the aldehyde type of oxycellulose contradicts this general rule. It must, therefore, be concluded that the paradoxical behavior of the oxycellulose can be understood only by the assumption that during the reaction with alkali the substance changes its structure in such a manner that the C—O—C "glycosidic" or "acetal" linkages lose their original character and become susceptible to hydrolysis. This conclusion leads directly to a consideration of the prototropic changes as the second type of transformation which may conceivably take place in alkaline medium.

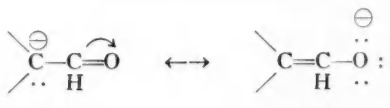
On account of the presence of $-\overset{|}{C}H-C=O$ groupings in the aldehyde type of oxycellulose, theo-



(IX)

retically the substance (I) is in equilibrium with the tautomeric enol-form (IX).

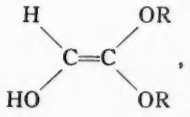
Such "hydroxymethylene" forms of the simple aldehydes like acetaldehyde, etc., are unknown. However, several aldehydes exist in this desmotropic modification, particularly if the carbon atom at the α-position to the carbonyl group carries electrophilic substituents. Glyoxal belongs to this category; it represents an equilibrium mixture of the keto-form and the tautomeric enol-form, $\overset{H}{HO}\!\!-\!\!C=C=O$, hydroxyketene. The enol-form is present to the extent of 27.8 percent. This follows from the C—C bond distance (1.47 Å.) in the ordinary glyoxal [12] and from the thermodynamical calculations of Williams, Symonds, Ekeley, and Ronzio [13]. In cases in which the groups attached to the α-carbon are strongly electrophilic, the molecule behaves as an acid and yields stable sodium salts. For instance, hydroxy-methylene-acetylacetone [14], $(CH_3 \cdot CO)_2 C=CHOH$, which is the diketo-enol-form of diacetyl acetaldehyde, $(CH_3CO)_2CH—CHO$, with its dissociation constant of $K = 0.0022$, is a stronger acid than acetic acid with the dissociation constant of $K = 0.0018$. This means simply that in the keto-form the hydrogen atom at the α-position to the carbonyl group has a more or less pronounced tendency to break loose as a proton from that carbon atom. The extent of this dissociation determines the "acidity" of the aldehyde and clearly depends, among other factors, upon the electrochemical nature of the groups attached to the α-carbon atom. In the presence of hydroxyl ion the proton will be removed to give water molecule, and the resulting anion is stabilized by the energy of resonance between the two mesomeric forms (X) and (XI).



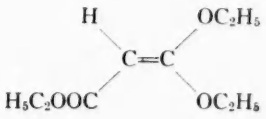
(X) (XI)

The enol-form of the aldehyde type of oxycellulose (IX) represents a dibasic acid. But the "acidity" develops—that is, the prototropic change occurs—only in the presence of hydroxyl ions; in neutral solution the equilibrium between the keto (I) and enol (IX) forms lies almost entirely in favor of the aldehyde molecules. A closer inspection of the enol formula (IX) reveals that of the two hydroxymethylene groups the one which belongs to the glyoxal part of the unit is different from the other, which belongs to the tetrose constituent.

The simplified formula for the glyoxal part of the unit,

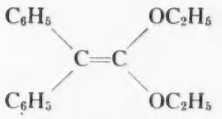


clearly shows the most significant fact—that the periodate oxycellulose and the other similarly built dialdehydes, on account of this glyoxal constituent, belong to the acetals of hydroxyketene. Now it is known from the literature that negatively substituted ketene acetals are very unstable compounds. They hydrolyze rapidly to the corresponding esters, even in pure water, by the loss of one alkoxy group —for instance, the ethylester of the diethylacetal of ketene carboxylic acid (XII) [15]



(XII)

hydrolyzes at room temperature in water to give ethyl alcohol and ethyl malonate, $H_5C_2OOC—CH_2—COOC_2H_5$. Similarly, Fritsch [16] found that diphenylketene diethylacetal (XIII)

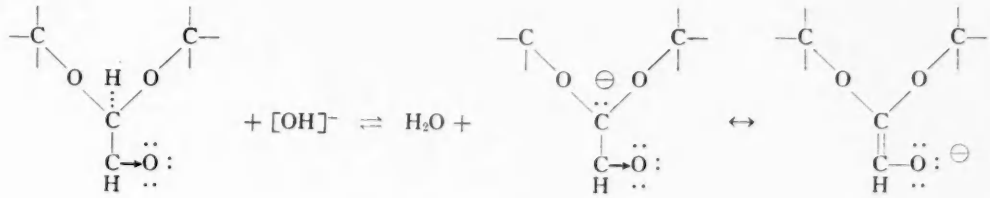


(XIII)

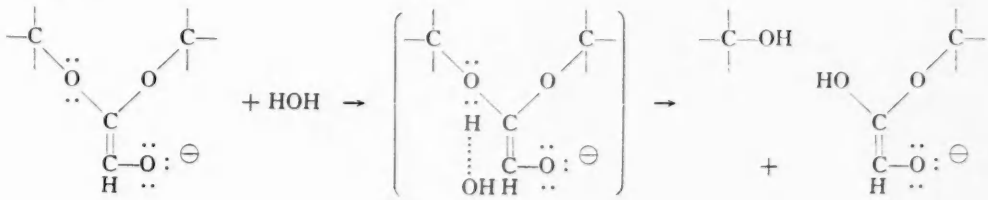
is evidently unstable in *alkaline* media and changes in the sodium salt of diphenylacetic acid, $(C_6H_5)_2CH—COONa$.

On the basis of the foregoing we believe that the aldehyde type of oxycellulose, being essentially a negatively substituted ketene acetal, hydrolyzes rapidly in alkaline medium to an ester of glycolic acid by the cleavage of either of the two C—O—C linkages. The ester so formed immediately undergoes a regular base-catalyzed hydrolysis. The following equations should give a comprehensive picture of the steps involved in the reaction of the glyoxal part of periodate oxycellulose.

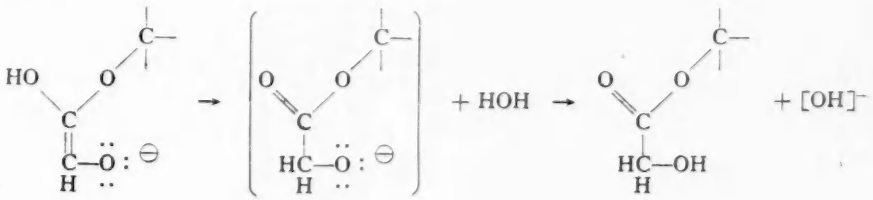
*First step:*



*Second step:*



*Third step:*



In the first step, the α-proton is removed by the hydroxyl ion of the alkali with the production of the mesomeric oxycellulosate ion. In the second step, the enolate ion, being essentially of a ketene acetal type, is cleaved by an electrophilic attack of the water molecule, which, by a displacement mechanism, breaks one of the C—O—C linkages to yield the enol-form of glycolic acid ester. The third step illustrates the prototropic change of the enol-form of the ester to the normal keto-form and the regeneration of the catalyst, $[OH]^-$. The latter is subsequently consumed in the rapid hydrolysis of the ester through the well-known mechanism for base-catalyzed hydrolysis. This process gives rise to the sodium salt of glycolic acid and *D*-erythrose. It is to be noted that the extent of the cleavage depends upon the position of the equilibrium in the first step —that is, on the "acidity" of the starting material. In the simple dialdehydes (VII and VIII), where one of the two OR groups represents a methoxyl instead of an erythrose residue, the acidic character of the molecule is apparently much less pronounced than in the periodate oxycellulose. This follows from Fry, Wilson, and Hudson's and from our experimental results, which would seem to indicate that in the former molecules (VII and VIII) the anionotropic changes leading to the Cannizzaro type of reaction occur to a considerable extent. Of course, both the anionotropic and the prototropic changes may take place simultaneously as competing reactions. Furthermore, the erythrose liberated in the cleavage of oxycellulose is subject to the numerous reversible and irreversible changes which the reducing sugars undergo in alkaline media. It is known from Nef's calculations that in an alkaline solution of a hexose theoretically not less than 113 different substances might be present. The isolation and identification of all the primary and secondary scission products present in the alkaline solution of oxycellulose appears to be a formidable task. We are fully aware of the fact that the validity of our hypothesis, which is at present supported only by indirect evidence, hinges on the formation of glycolic acid. Since the separation of the previously mentioned crystalline brucine salts has not yet been accomplished, at present we cannot state whether or not glycolic acid did form in the alkaline hydrolysis of the periodate oxycellulose.

On the basis of our working hypothesis the ageing of alkali cellulose can also be interpreted. We believe that most of the oxidizing agents used in cellulose chemistry, oxygen in alkaline media being one of them, attack the glucose anhydride units of cellulose in the same fashion as periodic acid does. The attack first occurs on the amorphous area of the fiber and produces the dialdehyde type of glucose anhydride units, which are at once cleaved in alkali through the mechanism which has just been outlined. The result is a cellulose with shorter chains and more end groups, and hence with higher copper number and lower viscosity. Evidently, complete elimination of the aldehyde type of oxidation by the use of suitable bleaching or oxidizing agents and restriction of the attack to the amorphous region of the cellulose should result in improved fibers, which would not deteriorate rapidly in even mildly alkaline medium, such as a soap solution. On the other hand, if the employment of a bleaching or oxidizing agent which produces the aldehyde type of oxycellulose is unavoidable, then the use of some neutral or slightly acidic detergent instead of soap would be most advantageous.

## Summary

1. It has been pointed out that contrary to widespread belief, the aldehyde type of oxycellulose which structurally belongs to the semiacetals of glyoxal is not affected by treatment with cold acid to any appreciable extent.

2. It has been found that oxidation of periodate oxidized cellulose by bromine in sodium bicarbonate solution, followed by acid hydrolysis, gives rise to a 75 percent yield of glyoxylic acid isolated as 2,4-dinitrophenylhydrazone.

3. It has been pointed out that the consumption of alkali by periodate oxidized cellulose is not due to carboxylic groups; it is caused by certain anionotropic and prototropic changes which may take place as competitive reactions.

4. Of the anionotropic changes the Cannizzaro type of reaction, previously found by other investigators, has been studied under modified conditions on the dialdehyde obtained by periodate oxidation of α-methyl-*D*-glucopyranoside.

5. In connection with the prototropic changes, a hypothesis based on the electron concept of valence has been presented to explain the easy cleavage by

alkali of the C—O—C bonds of the aldehyde type of oxycellulose, and to interpret the ageing of alkali cellulose.

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6. Harries, *Ber.* **36**, 1935 (1903).
7. Helferich and Russe, *Ber.* **56**, 763 (1923).
8. (*a*) Fischer and Geuther, *Ztschr. f. Chem.* **7**, 270 (1864); *Jahresber. fortschr. Chem.*, 316 (1864); (*b*) Blaise and Picard, *Compt. Rend.* **152**, 960 (1911); (*c*) Pucher, *J. Am. Chem. Soc.* **42**, 2258 (1920).
9. Pinner and Klein, *Ber.* **11**, 1478 (1878).
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14. Claisen, *Ann.* **297**, 6, 59 (1897).
15. Reitter and Weindel, *Ber.* **40**, 3360 (1907).
16. (*a*) Fritsch, *Ann.* **297**, 318 (1897); (*b*) Fritsch and Feldmann, *ibid.* **306**, 74 (1899).


# Annual Meeting of the Institute

FRIDAY, November 9, is the date set for this year's annual meeting of Textile Research Institute, Inc.

The meeting will be held in New York at the Waldorf Astoria Hotel, commencing with a business meeting for Institute members at 9:00 A.M. The morning technical session from 10:30 to 12:30 will be devoted to the fundamental research work of the Textile Foundation at Princeton, New Jersey, in which five T.R.I. graduate fellows are participating. Reports will be given of research concerned with the mechanical properties of textiles and also on the oxidative degradation of cellulose. In connection with the latter subject some important conclusions have been reached with respect to the action of soaps and other detergents on oxidized cellulose.

Luncheon will be served at 12:45 and will be followed by an address by Prof. H. D. Smyth, Chairman of the Department of Physics of Princeton University, who is the author of the official report on the development of the atomic bomb. His subject will be "Atomic Energy."

The afternoon session, commencing at 2:30, will be devoted to a technical program conducted by the research staff of the Institute. The papers will include the following subjects: "A Method of Correlation of Equilibrium Moisture Regain in Textile Fibers: Theoretical and Industrial Implications" and "Progress Report on Radiation Drying of Textiles."

Members of the Institute will receive formal notice of the meeting and the detailed program. Non-members are welcome to attend the technical sessions and luncheon. Those who are interested may obtain information by writing to the Textile Research Institute, Inc., 10 East 40th Street, New York 16, N. Y. Luncheon tickets will be $5.00 and should be obtained in advance.

# Selected References on Surface Chemistry and Physics

**Agnes S. Dyer* and Earl K. Fischer****

*This specialized bibliography is the first of its kind to appear in* TEXTILE RESEARCH JOURNAL. *It was prepared to offer a listing of books and other primary references in a restricted field of inquiry which would serve as the basis for the accumulation of a company or personal library.*

*Similar treatment of other subjects is planned for future issues, and the Editor invites readers to send their comments on this type of expansion of the literature service offered by the* JOURNAL, *particularly with respect to other fields of scientific, technological, manufacturing, and economic research with which the textile industry is concerned.*

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THE subject, surface chemistry and physics, represents in several respects a specialized branch of physics and physical chemistry and may be considered as part of the larger field of colloid chemistry. In order to keep the number of references within a practicable and useful dimension, a relatively large number of the books and monographs in the original listing have been omitted. It is believed that the ones included in the listing below adequately cover the field as it has been limited, and should serve as a foundation reference list of the literature.

The actual selection of items was based on several criteria, but the chief factor was availability of the volumes, either by purchase from publishers and book dealers, or for reference in the larger technical and scientific libraries. Review articles which appeared in periodicals were excluded, not because these were considered of less value but because such reviews are seldom available as separate publications.

## Monographs

1. Adam, Neil Kensington, *Physics and Chemistry of Surfaces,* 3rd Edition. 424 pages. Oxford, Clarendon Press, 1941.

This well-known book covers the whole field of surface phenomena. Topics include surface films, adsorption, molecular shape and size, surface-tension measuring methods, spreading and lubrication, catalysis, electrification at interfaces. The description of film-balance techniques is noteworthy.

2. Bakker, Gerrit, *Kapillarität und Oberflächenspannung.* 458 pages. Leipzig, Akademische Verlagsgesellschaft, 1928.

This monograph provides a detailed exposition of the general field. Many of the topics covered are based on the original papers of research workers, with each section a discussion of the results of the different authorities.

3. Bouasse, Henri P. M., *Capillarité: Phenomenes Superficiels.* 437 pages. Paris, Librairie Delagrave, 1924.

The mathematics of surface phenomena are treated in detail and illustrated with 232 diagrams. Part of the book is devoted to theory underlying applications, such as adsorption, soaps, emulsions, spreading, etc. The book is deficient in references.

4. Burdon, R. S., *Surface Tension and the Spreading of Liquids.* 85 pages. Cambridge University Press (New York, Macmillan Co.), 1940.

This is a small book with brief topical discussions of surface-tension measurement and data, spreading on water and mercury, liquids on solids, the nature of surface forces. With its emphasis on anomalies and fields for further research, this volume provides stimulating reading, but it is not intended to be a comprehensive treatment.

* Michigan State College, East Lansing, Michigan.
** Institute of Textile Technology, Charlottesville, Virginia.

5. Chwala, August, *Textilhilfsmittel: Ihre Chemie, Kolloidchemie, und Anwendung.* Vienna, Julius Springer, 1939 (reprinted by Edwards Brothers, Inc., Ann Arbor, Mich., 1943).

This is a valuable treatise on the chemistry of textile assistants (including surface-active substances), with detailed discussion of their application in the manufacture and processing of textiles. The text is well documented with references to the original research papers.

6. Clayton, William, *The Theory of Emulsions and Their Technical Treatment,* 4th Edition. 482 pages. Philadelphia, Blakiston Co., 1943.

Although this book is intended to cover the special topic of emulsions, the first part contains an extensive review of experimental and theoretical work on the more general subject of surface phenomena. It is well documented with citations to the original literature. The fourth edition supplements the appendix to the patent citations in the third (1935) edition.

7. Defay, Raymond, *Etude thermodynamique de la Tension Superficielle.* 355 pages. Paris, Gauthier-Villars and Co., 1934.

A detailed study is given of the thermodynamics of surface phenomena.

8. Dorsey, N. Ernest, *Measurement of Surface Tension.* 33 pages. Washington, National Bureau of Standards, Scientific Paper 540, Bulletin 21, pp. 563–95, 1926.

A detailed review of the methods of surface-tension measurement, with critical evaluation of these methods and the underlying theory. The paper contains a bibliography of 110 references.

9. Freundlich, H., *Kapillarchemie,* 3rd Edition, 2 volumes (1,181 pages), 1923–1924. 4th Edition, 2 volumes (Vol. 1, 566 pages, 1930; Vol. 2, 955 pages, 1932). Akademische Verlagsgesellschaft. m.g.H. English translation from the 3rd German Edition by H. Stafford Hatfield (883 pages), London, Methuen & Co., 1926.

This is the standard reference book on surface and colloidal phenomena.

10. Hartley, G. S., *Aqueous Solutions of Paraffin-Chain Salts.* (Actualités Scientifiques et Industrielles No. 387.) 70 pages. Paris, Hermann & Cie, 1936.

A qualitative and semi-quantitative description of the internal nature of aqueous solutions of soaps and detergents.

11. Lloyd, John Uri, and Waldbott, *References to Capillarity to the End of the Year 1900.* 212 pages. Bulletin, Lloyd Library of Pharmacy, Cincinnati, Ohio, 1902.

This is a useful and interesting bibliography of the important early publications on surface phenomena. References begin with the earliest records (*circa* 1600) and total 665 by 1900. Each citation is followed by a brief abstract. Completely cross-indexed by topics.

12. du Nouy, P. Lecomte, *Surface Equilibria of Biological and Organic Colloids.* 193 pages. American Chemical Society monograph, Chemical Catalog Co., Inc. (New York, Reinhold Publishing Corp.), 1926.

This monograph describes the author's work in detail. Contains an extensive bibliography of journal articles.

13. Rideal, Eric Keightley, *An Introduction to Surface Chemistry,* 2nd Edition. 450 pages. Cambridge University Press (New York, Macmillan Co.), 1930.

This is one of the well-known reference volumes covering the field.

14. Valko, E., *Kolloidchemische Grundlagen der Textilveredlung.* 701 pages. Berlin, J. Springer, 1937.

Chapter 14 (pages 519–581) provides a review of the physical chemistry of the solutions of soaps and synthetic detergents. Chapter 15 (pages 581–646) describes the wetting, emulsification, and detergency phenenomena in relation to the treatment of textiles. Extensively documented by tables, charts, and bibliography.

### Collective Works

15. *Advances in Colloid Science,* Vol. I. Elmer O. Kraemer, Editor. New York, Interscience Publishers, 1942.

This volume is the first of a series. Of particular interest are the following two articles:

"Solubilization and Other Factors in Detergent Action," J. W. McBain, pp. 99–142.

"Anomalies in Surface Tension of Solutions," E. A. Hauser, pp. 391–415.

16. *Colloid Chemistry—Theoretical and Applied.* Jerome Alexander, Editor. Chemical Catalog Co., Inc. (New York, Reinhold Publishing Corp.).

Volume I: Theory and Methods, 1926.

"Surface Energy and Surface Tension," William D. Harkins, pp. 192–264.

"Surface Tension of Colloidal Solutions and Dimensions of Certain Organic Molecules," P. Lecomte du Nouy, pp. 267–75.

"Surface Films as Plastic Solids," R. E. Wilson, pp. 276–7.

"Friction, Surface Energy, and Lubrication," W. B. Hardy, pp. 288–305.

"Attraction Intensity or Attraction Pressure," J. Traube, pp. 640–6.

Volume II: Biology and Medicine, 1928.

"The Surface Tension of Colloids with Special Reference to Protein Colloids," Fil. Bottazzi, pp. 121–63.

"The Modifications of the Dynamic Surface Tension of Plasma and Serum," E. Zunz, pp. 651–84.

Volume III: First Series of Papers on Technological Applications, 1931.

"Wetting of Solids by Liquids," F. E. Bartell, pp. 41–60.

Volume IV: Second Series of Papers on Technological Applications, 1932.

"Alkaline and Other Detergents: Their Function in Laundering, Textile Processing, and General Cleansing Operations," H. G. Elledge, pp. 635–52.

"The Colloid Chemistry of Washing," L. Zakarias, pp. 653–66.

Volume V: Theory and Methods, Biology and Medicine, 1944.

"The Surfaces of Solids and Liquids and the Films That Form Upon Them," William D. Harkins, pp. 12–101.

"Solutions of Soaps and Detergents as Colloidal Electrolytes," James W. McBain, pp. 102–20.

Volume VI: (In press).

17. *Recent Advances in Surface Chemistry and Chemical Physics.* Forest Ray Moulton, Editor. American Association for the Advancement of Science, Publication No. 7. Lancaster, Pa., Science Press, 1939.

The papers in this volume which deal primarily with surface phenomena emphasize biological applications.

18. *Surface Chemistry.* Forest Ray Moulton, Editor. American Association for the Advancement of Science, Publication No. 21, 160 pages. Lancaster, Pa., Science Press, 1943.

Ten papers which deal with subjects of current research interest are included in this volume.

19. *Reports on Colloid Chemistry and Its General and Industrial Applications* (publications of the British Association for the Advancement of Science).

First Report, 1917.

Second Report, 1918.

"Colloid Chemistry in the Textile Industries," W. Harrison, pp. 52–69 (with bibliographies).

Third Report, 1921.

"Colloid Chemistry of Soap. Part I—Solutions," J. W. McBain, pp. 2–31.

Fourth Report, 1922.

"Molecular Attraction and Physical Properties of Liquids," E. Edser, pp. 40–113.

Fifth Report, 1923. (Includes author and subject index for the five reports.)

"The Measurement of Surface Tension," Allan Ferguson, pp. 1–12. (Bibliography of 53 references.)

"Industrial Application of Wetting Power," W. H. Nuttall, pp. 38–46. (Bibliography of 43 references.)

20. "Capillary Action," *Encyclopaedia Britannica*, 11th Edition, 1910–11.

This article, revised by Lord Rayleigh (3rd Baron), was based on the previous *Britannica* articles by James Clerk Maxwell. It includes an extended mathematical and theoretical discussion of the subject with definitions and illustrative data.

"Surface Tension," *ibid.*, 14th Edition, 1930.

This article was prepared by Alfred W. Porter and is based in part on the previous *Britannica* articles.

21. *International Critical Tables.* New York, McGraw-Hill Book Co., 1926–1933.

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"Surface Tension Data of Elements in Liquid State," Vol. I, p. 103.
"Tensile Strength and Angle of Contact," Vol. IV, p. 434.
"Methods of Measuring Surface Tension," Vol. IV, p. 435.
"Interfacial Tension for Solid-Liquid and Liquid-Liquid Interfaces," Vol. IV, pp. 436–9.
"Surface Tension of Metals," Vol. IV, pp. 439–40.
"Surface Tension and Related Properties for Temperatures Below 0°C," Vol. IV, pp. 441–2.
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"Properties of Thin Films and Surface Layers," Vol. IV, pp. 475–7.
"Surface Tension of Soap Solutions," Vol. V, pp. 449–50.

22. *Comprehensive Treatise on Inorganic and Theoretical Chemistry,* J. W. Mellor, Vol. I, pp. 846–60. London, Longmans, Green & Co., 1922.

A summary correlating surface-tension data with other physical properties. The article is well documented.

23. *Conference on Surface-Active Agents.* New York Academy of Sciences. Publication is scheduled for Volume 46 of the *Annals of the New York Academy of Sciences* (1945 or 1946).

Titles of the papers presented at the conference held in January, 1945, follow:

"The Structure and Properties of Solutions of Colloidal Electrolytes," A. W. Ralston.
"Surface-Active Agents at Interfaces," Earl K. Fischer and David M. Gans.
"Certain Aspects of the Chemistry of Surface-Active Agents," Donald Price.
"Properties Involving Surface Activity of Solutions of Paraffin-Chain Salts," Leo Shedlovsky.
"Surface-Active Agents in Biology and Medicine," E. I. Valko.
"The Nature of the Bactericidal Action of Surface-Active Agents," Rollin D. Hotchkiss.
"Surface-Active Agents in Industry," R. R. Ackley.
"Surface-Active Agents in Ore Flotation," M. D. Hassialis.

24. *Wetting and Detergency Symposium.* 207 pages. London, A. Harvey (New York, Chemical Publishing Co.), 1937.

This group of papers was presented at a symposium held by the British Section of the International Society of Leather Trades Chemists in February, 1937. The authors represent various scientific and industrial fields. The volume is frequently cited.

25. *The Oil/Water Interface.* Transactions of the Faraday Society, Vol. 37, Part 3, March, 1941.

A general discussion held by the Faraday Society, January 9, 1941. Eleven papers.

26. *Physical Methods of Organic Chemistry,* Vol. I. Arnold Weissberger, Editor. New York, Interscience Publishers, Inc., 1945.

"Determination of Surface and Interfacial Tension," William D. Harkins; and "Parachor," George W. Thompson (Chapter VI), pp. 149–209.
"Determination of Properties of Monolayers and Duplex Films," William D. Harkins (Chapter VII), pp. 211–52.

# ABSTRACTS

*SERVICES AVAILABLE*

*Reprints of the original articles abstracted in* TEXTILE RESEARCH JOURNAL *are often available from the publishers. Otherwise, it may be possible to secure copies of the periodicals. A list of periodicals, the abbreviations used in references to articles, and the addresses of publishers of English language publications was given on page 22 of the January, 1945, issue. Orders should be sent direct to the publishers.*

*Photostat negatives of articles abstracted will be furnished to members of the Institute at a cost of 15 cents per page for pages not exceeding 7 inches in width and 25 cents per page for larger sizes up to 11½ x 14 inches. Photostats of patents are 25 cents a page. Postage will be added.*

*Microfilm copies and paper enlargements of microfilm may be obtained from: Microfilms Inc., 313 N. First St., Ann Arbor, Mich.; New York Public Library, New York, N. Y.; Yale University Library, New Haven, Conn.; Harvard University Library, Cambridge, Mass.; and Library of Congress, Washington, D. C. Translations may also be obtained from the above sources.*

## ANALYSIS: TESTING: LABORATORY METHODS

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### Alkyl Amines

**Laboratory preparation of alkyl amines.** J. B. Dickey. *Syn. Org. Chemicals* **17**, No. 2, 1–6 (1945).

Practical methods for the preparation of alkyl amines are classified and equations for numerous examples of each class are given. Altogether, equations are given for the preparation of 49 different alkyl amines. A. R. Martin

### Crystallinity of Cellulose

**Chemical characterization of rayon yarns and cellulosic raw materials.** C. C. Conrad and A. G. Scroggie. *Ind. Eng. Chem.* **37**, 592–8 (June 1945).

Nickerson's method for the hydrolysis and catalytic oxidation of cellulosic materials by means of HCl and $FeCl_3$ has been modified to reduce superheating and minimize the differences in boiling point due to changes in pressure. The new apparatus which is described gives more reproducible results. Glucose is used as a standard, and carbon dioxide time curves for cotton linters and high viscosity rayon are determined. With glucose there is an induction period in which small amounts of $CO_2$ are produced at a steadily increasing rate, probably because of the formation of an intermediate upon which the production of $CO_2$ depends. An abrupt drop in rate of evolution of $CO_2$ occurs after about 1 mole of $CO_2$ per mole of glucose. This occurs after 10 hrs. The reaction is not complete in 50 hrs. Nickerson's "% amorphous cellulose" is redefined as "% accessibility." Three methods of calculating accessibility are given. The accessibility of cotton linters and wood pulps generally decreases with increasing alpha-cellulose content. Accessibility of viscose rayons with grams-per-denier strength from 1.8 to 4.9 vary from 27 to 15%. High-tenacity deacetylated cellulose acetate gives a strength of 4.2 g. per denier and accessibility of 16.5%. Crystallinity numbers as calculated from intensity measurements of x-ray diffraction patterns increase as accessibility percentages decrease. A. R. Macormac

### Color-Blindness

**Tests for the detection and analysis of color-blindness. III. The Rabkin test.** LeGrand H. Hardy, Gertrude Rand, and M. Catherine Rittler. *J. Opt. Soc. Am.* **35**, 481–91 (July 1945).

This paper is another in the series evaluating various color-blindness tests on the basis of work being done in the Knapp Memorial Laboratories, Institute of Ophthalmology, College of Physicians and Surgeons, Columbia University. D. Nickerson

### Identification Stain for Fibers

**A new stain for identifying papermaking fibers.** Norval F. Wilson. *Paper Ind. Paper World* **27**, 215–16 (1945) (through *Chem. Abstr.* **39**, 3664[7] (Aug. 20, 1945)).

The stain is prepared as follows: I crystals 0.8 grams, $CdI_2$ 35.0 grams, distilled water 50.0 cc.; when solution is complete at 110°F, add the following in order: distilled water 90 cc., formaldehyde 7 cc., $Ca(NO_3)_2 \cdot 4H_2O$ 70 grams, $CdCl_2 \cdot 2\frac{1}{2}H_2O$ 20 grams. Colors produced on the chief papermaking fibers are: soda, purple; linen rag, pink; kraft, brown (some gray); ground-wood, yellow; unbleached sulfite, colorless; bleached sulfate, blue; bleached sulfite, lavender; cotton, red; straw, green predominates. A sample for examination is conveniently prepared by cutting out with a small hand punch disk samples about 3/16 in. in diameter from the sheet to be examined, disintegrating by shaking in a miniature ball mill consisting of a stoppered test tube containing a few glass beads and the proper amount of distilled water as determined from the weight of the sample.

### Moisture Determination

**Electrometric end-point for Fischer reagent moisture determination.** R. P. Rennie and J. L. Monkman. *Can. Chem. and Proc. Ind.* **24**, 366–70 (May 1945).

A general method has been developed for the determination of mois-

ture in various materials by means of the Karl Fischer reagent. An electrical unit combining end-point indicator, cell, and electrode system has been designed and has proved to be satisfactory for this purpose. The method is applicable to both high and low ranges of moisture content. The method is applicable to opaque and colored solutions such as shellac, thereby overcoming the limitations of the visual end-point. The method is considerably more rapid than many of the currently used procedures for moisture estimations, such as oven drying. Detailed methods have been described for the determination of moisture content of gunpowder, glacial acetic acid, commercial sawdust, and shellac solution. Use has been made of a hydrated salt (ammonium oxalate) for the standardization of reagents. This method is considerably more convenient than the use of weighed water samples and is more rapid.

Author

## Photography in Textile Research

**Photography as applied to textile research.** C. W. Bradley. *J. Soc. Dyers and Colourists* **61**, 61–3 (Mar. 1945).

In addition to providing permanent records of passing events, photography is a useful research tool because of its ability to integrate weak light, to utilize spectral wave lengths outside the range of human vision, and to record motion. Some interesting applications of photography in textile research which are described are the preparation of low-power stereo-micrographs, ultraviolet, infra-red, and fluorescence photography, motion photography with a still camera by means of an oscillograph, and high-speed motion photography with a motion picture camera using an electric spark light source ("spark cinematography"). Photographs produced by use of these techniques are shown. C.

## Analysis of Plastics

**Analytical aspects of plastics—Part III.** Harry Barron. *Brit. Plastics* **17**, 56–62 (Feb. 1945).

Some qualitative methods are given for distinguishing the cellulosic plastics, polystyrene, poly-acrylic and methacrylic esters, polyvinyl chloride, and the common plasticizers. Procedures are also given for the estimation of acetyl content and free hydroxyls in cellulose derivatives, strength of acetic anhydride, nitrogen and camphor content of cellulose nitrate plastics, dibutyl phthalate, tricresyl phosphate, calcium stearate, and white lead. The preceding two parts were published in the Aug. and Oct., 1944, issues of *Brit. Plastics*.

E. F. Evans

## Spectrophotometry

**Analytical representation of trichromatic data.** Parry Moon and Domina Eberle Spencer. *J. Opt. Soc. Am.* **35**, 399–427 (June 1945).

The authors have developed equations based on the C.I.E. (or I.C.I.) functions of $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, and $\bar{z}(\lambda)$. At present all work done with these colorimetric functions must be done from tabulated values. The proposed method allows many mathematical treatments not now convenient or possible. The authors claim an accuracy near the center of the diagram that "gives results that agree with C.I.E. values to within the experimental error of the best visual measurements." For the highly chromatic samples studied there are discrepancies, but it is indicated that they are not larger than those resulting from use of the selected ordinate method under extreme conditions. (Abstractor's Note: This must refer to use of 30 ordinates, since the selected ordinate method will provide any degree of accuracy required, depending upon the number of ordinates used.) The authors give results for several other tests of accuracy. The proposals made by Moon and Spencer are stimulating to further research; they should not, however, be used in substitution for I.C.I. adopted values for colorimetric functions. One detail worth noting and clarifying is the suggestion that the units associated with $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, and $\bar{z}(\lambda)$ be named Munsell, Young, and Ostwald. Since the color contributions of Munsell and Ostwald are in a field quite apart from trichromatic colorimetry, enough objection has been made to the use of their names in this connection that the authors, it is understood, will find other names to be associated with that of Young in identifying these three trichromatic units.

D. Nickerson

**Uses of retardation plates in spectrophotometry.** George L. Buc and E. I. Stearns. I. **Determination of slit shape and slit width,** *J. Opt. Soc. Am.* **35**, 458–64 (July 1945); **II. Calibration of wave-length,** *ibid.*, 465–70; **III. Measurement of dichroic samples,** *ibid.*, 521–4 (Aug. 1945).

There is a general trend toward recognition of the fact that if spectrophotometric data from different laboratories and different instruments are going to be compared, it is necessary to specify the exact conditions of measurement, which includes a description of the slit used. These articles, which are three of a single series, describe a method developed in the laboratories of the Calco Chemical Division of the American Cyanamid Company for evaluating slit width on a performance basis. A retardation plate is used to make a "calibrator" having a known transmission curve. The articles describe the calibrator and its use.

D. Nickerson

# CHEMICAL AND PHYSICAL RESEARCH

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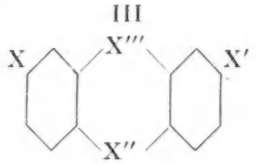
## Absorption Spectra of Dyes

**Rules for the absorption spectra of dyes.** Gilbert N. Lewis. *J. Am. Chem. Soc.* **67**, 770–5 (May 1945).

The main X band of dyes with the skeleton formula III belonging to six great classes of dyes is determined by two rules. The first, theoretical, states that lambda is always greater, the greater the fraction of the characteristic positive charge that is on the auxochromes. The second, empirical, states that the effect upon lambda of various groups is additive. In formula III, X and X′ are auxochromes and identical. X″ is

either C R or N. X''' may be O, S or N R or may be absent. Observed and calculated lambdas show an average difference of less than 5 mμ for triphenylmethane, xanthene, diphenylmethane, oxazine, thiazine, and azine dyes. The difference in the case of the acridine dyes is probably due to the fact that the calculated values are for the second or y band.

III




A. R. Macormac

## Acetylation of Cellulose

**The acetylation of cellulose.** Francisco A. Bertuzzi, S. A. Suarez, O. Elizaga, and R. Kamachi. *Rev. facultad quim. ind. agr.* (Univ. nacl. litoral Santa Fé, Argentina) **9/10**, 63–70 (1940–1941) (Pub. 1942) (through *Chem. Abstr.* **39**, 2647[7] (June 20, 1945)).

Data are presented on the effects of variation in time and temperature on the acetylation of cellulose (**I**) and of variations in concentration of the catalytic agents and of time on the hydrolysis of the polyacetate (**II**). The process is predicated on the assumption that the best method for the preparation of a moderately acetylated **I** consists of overacetylation and subsequent hydrolysis to the desired product. Cotton (5 g.) is added to 20 cc. AcOH containing 0.2 cc. $H_2SO_4$ (d. 1.84). In the course of an hr. 13.8 cc. $Ac_2O$ is added. The temperature is kept between 10° and 40°. When all the **I** is dissolved (a clear liquid), it is hydrolyzed with 29 cc. of a mixture of 90 cc. $H_2O$ and 10 cc. $H_2SO_4$ (d. 1.84). Precipitation of the diacetate (**III**) takes place during 12 hrs. on addition of water with strong agitation. The Ac group was determined by dissolving 1 g. of **III** in 50 cc. acetone and saponifying with 10 cc. *N* NaOH, with agitation. After 24 hrs. 10.5 cc. *N* $H_2SO_4$ was added, with agitation for 0.5 hr. The excess acid was titrated with 0.1 *N* NaOH. The results were expressed as AcOH and checked against a blank. In 7 acetylations the Ac content (expressed as $CH_3COOH$) varied from 60.1% for 150 min. to 67.8% for 1,365 min. It required 1,680 min. for complete disappearance of the fibers at 20° and only 50 min. at 60°. In the hydrolysis for 12 hrs. at 40°, 55.8% Ac resulted with 1 cc. of catalyst and 42.8% for 5 cc. Samples acetylated for 12 hrs. at 40° were immediately hydrolyzed with NaOH for various lengths of time. After 130–310 min. the content of AcOH was 64%; after 370 min., 65.2%; after 1,450 min. 46.9%. Maximum solubility in acetone (96.6%) was obtained for **III** prepared by acetylation at 60° for 50 min.

## Water Adsorption of Proteins

**The adsorption of water by proteins.** Linus Pauling. *J. Am. Chem. Soc.* **67**, 555–7 (Apr. 1945).

The data published by Bull and other investigators on the adsorption of water by proteins can be in considerable degree interpreted on the assumption that the initial process is the attachment of one water molecule to each polar amino acid side chain. The data also indicates that peptide carbonyl and imido groups usually do not bind water because of their mutual interaction by hydrogen-bond formation, but that water is bound by carbonyl groups which are not coupled by hydrogen bonds with imido groups. In salmine, in which most of the amino-acid residues are polar, these polar residues cooperate to attach one water molecule jointly to two polar groups in the initial process of hydration. Author

## X-Ray Diagram of Buna-S

**The x-ray diagram of a Buna-S vulcanizate.** R. E. Morris and C. B. Jordan. *Rubber Chem. Tech.* **18**, 20 (Jan. 1945).

Failure of other investigators to find any trace of fiber pattern in x-ray diagrams of Buna-S, either unstretched or stretched, is attributed to the irregular molecular structure of Buna-S. The authors have obtained x-ray evidence of some degree of orientation in highly stretched Buna-S vulcanizate. Two x-ray diagrams are shown. W. E. Davis

## Degradation of Rubber

**Physical and chemical degradation of rubber.** D. F. Twiss. *Nature* **156**, 9–11 (July 7, 1945).

A summary of the contents of nine papers constituting a symposium of the Midland Section of the Institute of the Rubber Industry, held on May 12, 1945. H. W. Theller

## Cellulose Dispersions

**Conversion of cellulosic materials into viscose by the emulsion method for the determination of the xanthate viscosity and the mean degree of polymerization. I. Development of a new measuring technique.** G. Jayme and J. Wellm. *Kolloid-Z.* **107**, 163–80 (June, 1944). (In German) (through *Bull. Inst. Paper Chem.* **15**, 401, July, 1945).

The emulsion method of Jayme and Grogaard (cf. B.I.P.C. **10**: 475), in which the cellulosic material is directly dispersed in strong aqueous alkali and carbon disulfide by shaking (instead of allowing alkali cellulose, prepared in the usual way, to react with carbon disulfide in a separate step), has been improved. Preswelling of the cellulosic material in water facilitates subsequent defibration in a 14–15 vol.-% sodium hydroxide solution. Finest subdivision in the mixture of the carbon disulfide (of which so much is employed that the required degree of xanthation is reached within a reasonable time for both easily and more slowly reacting wood pulps) is attained by adding a small amount of abietic acid. This equalizes the different reactivities of pulps of low and high resin contents and accelerates the substitution reaction. The fall in viscosity during the entire reaction, comprising xanthation and dissolution of the xanthate in the aqueous alkali, is governed essentially by the degree of mechanical agitation employed. In addition, the presence of oxygen (air) causes the viscosity to decrease with time.

This influence may be reduced so that it exerts a minor influence upon the final viscosity results by the addition of glucose to the emulsion, which is considerably simpler than carrying out the reaction in nitrogen. There is no mutual interference between the effects of glucose and abietic acid; rather, the effects are additive. The viscosity-concentration relationship is influenced by the chain-length distribution of the pulp or of mixtures of pulps of high and low viscosities, because of the different concentrations of the individual chain molecules in the solution. To eliminate this influence from the calculation—i.e., to express the viscosity-concentration relationship as a function of the average chain length of the mixture, independent of the distribution—the eighth-power formula of Philippoff and Hess (cf. *Z. physik. Chem.* **B 31**: 237–55 (1936)) is more suitable than others tested, the agreement between the calculated values and those experimentally determined on single pulps of varying (cuam) viscosity and of mixtures thereof and with staple fiber rayon being quite satisfactory. The degrees of polymerization, determined by the xanthate method, using the Hess and Philippoff formula, are in good agreement with those derived from the specific viscosities of the pulps in cuprammonium hydroxide solution using the Staudinger function. The xanthate values show less variation than the cuam values. The xanthate method is described in detail. 26 references.

## Anisotropy of Rubber

**The magnetic anisotropy of stretched rubber as a function of the tension to which it is subjected.** E. Cotton-Feytis. *Rubber Chem. Tech.* **18**, 8 (Jan. 1945).

The method used to determine the magnetic anisotropy is described briefly. With increase in degree of stretching the anisotropy also increases, but finally approaches a limiting value. This behavior parallels the change in intensity of x-ray diffraction spots on the stretching of rubber, and is attributed to the same cause—namely, the progressive orientation of molecular chains in parallel formation. W. E. Davis

## Hydrolysis of Cellulose

**The hydrolysis of cellulose materials; present state and future prospects.** Ch. Bertholot. *Carburants nat.* **4**: 112–14 (1943); *C. A.* **38**: 6551 (1944). (In French; abstract in English. Abstract only available) (through *Bull. Inst. Paper Chem.* **15**, 437, July, 1945).

A general discussion of the acid hydrolysis of cellulose is presented. One metric ton of wood should yield theoretically 61.1% of sugar of the $C_6$ series (395 liters of alcohol) or 83.3% of sugar of the $C_6$ and $C_5$ series (275 kg. of ketones). Practically, 200 to 300 liters of alcohol are obtained. Hydrolysis of wood may be carried out to yield: molasses for feeding cattle; yeast according to the Bergius process; alcohol; ketones; lignin as a by-product; acetic and formic acids; acetone; and furfural. The chemistry of the hydrolysis of cellulose, the causes of poor yields, and means for improving the yield (e.g., by hydrolysis with formic acid) are discussed.

## Lignin

**Acetic acid spruce lignin and acetic acid Willstatter's spruce lignin.** F. E. Brauns and M A. Buchanan. *J. Am. Chem. Soc.* **67**, 645–9 (Apr. 1945).

Acetic acid spruce lignin and acetic acid Willstatter spruce lignin have been compared with isolated native spruce lignin. It is found that the number of hydroxyl groups in the acetic acid lignins is the same as that in the isolated native spruce lignin, indicating that no new hydroxyl groups are formed when lignin is extracted from spruce by means of acetic acid. Author

## Structure of Polyamides

**The macromolecular structure and drawings of a super-polyamide—nylon.** Georges Champetier and Jeanne Bonnet. *J. chim. phys.* **40**, 217–23 (1943); cf. Baker and Fuller, *C. A.* **37**, 4290[2] (through *Chem. Abstr.* **39**, 2653[4] (June 20, 1945)).

A fiber of polyhexamethylene adipamide was examined microscopically and by x-ray diffraction patterns at different degrees of drawing. The x-ray patterns showed the presence of a crystalline structure in the undrawn polyamide and that these crystalline elements became increasingly oriented as the fiber was elongated. The lack of high elasticity, as is found in stretched rubber, was attributed to H-bond formation between C=O and NH groups of neighboring chains. An identity period of 17.3 A. was determined from the diagram taken near the breaking point and agrees with the calculated value for a hexamethylene adipamide unit. Examination in polarized light revealed the presence of a network surface structure and poorly defined crystal spheroids of 5 $\mu$ maximum diameter within the fiber. These features disappeared with high orientation and the fiber showed nearly total extinction at right angles.

## High-Polymer Research

**Recent progress in high-polymer research.** H. Mark. *Record Chem. Progress* **6**, 1–6 (1945) (through *Chem. Abstr.* **39**, 3461[6] (Aug. 10. 1945)).

A review of research on the mechanism of polymerization, polymer behavior in dilute solution, structure and texture of some polymers, and some properties of cellulose. 94 references.

## Polymer-Plasticizer Interaction

**Polymer-plasticizer interaction.** Elizabeth M. Frith and R. F. Tuckett. *Nature* **155**, 164–6 (Feb. 10, 1945).

Summary of a discussion of current theories at the meeting of the Plastics Group of the Society of Chemical Industry, on Nov. 17, 1944.

H. W. Theller

## Polythene

**The properties and uses of polythenes—Part I.** E. Hunter and W. G. Oakes. *Brit. Plastics* **17**, 94–8 (Mar. 1945).

The polythenes are straight chain, paraffin polymers of ethylene exhibiting outstanding electrical properties, resistant to moisture and chemical attack and of great flexibility and toughness. They can be milled on heated rolls or in Bridge-Banbury-type mixers, injection molded, extruded, and used for dip coating. Data are given on their electrical and mechanical properties.
E. F. Evans

**The properties and uses of polythenes—Part II.** R. B. Richards. *Brit. Plastics* **17**, 146–51 (Apr. 1945).

Polythene, a linear polymer of ethylene, exhibits excellent chemical stability, low water permeability, and low solubility and swelling in organic liquids at temperatures below about 50°C. Its main use at present is as a cable dielectric. It can be obtained in the form of films, filaments (both yarn and monofils), powder for flame spraying, and aqueous dispersions. E. F. Evans

**The properties and uses of polythenes—Part III.** E. L. Midwinter. *Brit. Plastics* **17**, 208–15, 228 (May 1945).

Directions are given for the processing of polythene, including the optimum conditions of temperature, pressure, cooling, etc., for extrusion of cable coverings, tubes and films, molding by compression, injection and extrusion, hot melt coating, melt flowing and casting, powder spraying, solvent casting, and fabrication from sheets and tubes. Conforming to its chemically inert nature polythene is very resistant to "weathering," but at temperatures above about 120°C it oxidizes with a consequent increase in power factor and a change in the fluidity of the molten material. These changes are inhibited by the addition of a small amount of an antioxidant. Although polythene has been most extensively used for cable covering, its very low water vapor permeability and the relatively free flowing melt of some soft grades show value for paper and textile coatings.
E. F. Evans

## Specific Volumes of Proteins

**The partial specific volumes of zein and gliadin.** Joseph F. Foster and Dexter French. *J. Am. Chem. Soc.* **67**, 687–8 (Apr. 1945).

A dilatometer apparatus for use in the determination of partial specific volumes of prolamines in mixed solvents is described. The partial specific volume of zein is 0.776 and of gliadin 0.724. A. R. Macormac

## Reaction of Formaldehyde with Proteins

**The reaction of formaldehyde with proteins.** H. F. Conrat, M. Cooper, and H. S. Olcott. *J. Am. Chem. Soc.* **67**, 950–4 (June 1945).

In 4% solution, at pH 3 to 7 and 70° C, formaldehyde combined with both the primary amino and primary amide group of proteins. In contrast to interpretations of other investigators, the secondary amide linkages of the peptide chain and the phenolic groups were found not to bind appreciable amounts of formaldehyde. These findings were confirmed with protein derivative and synthetic polypeptides containing maximal and minimal numbers of reactive groups. The preparation of a polypeptide rich in primary amide groups from polyglutamic acid is described. This material bound more formaldehyde than did any of the proteins investigated.
Author

## Physical Measurements on Rayon

**Physical and chemical measurements on regenerated cellulose fibers.** Nils Gralen and Olof Samuelson. *Svensk Papperstidn.* **48**, 1–5 (1945) (English and German summaries) (through *Chem. Abstr.* **39**, 3157[1] (July 20, 1945)).

Measurements of the degree of polymerization (**I**) and of the polydispersity (**II**) of cellulose have proved of value for the determination of the quality of regenerated cellulose fibers. Two samples of staple fiber of different grades were studied by several physical and chemical testing procedures. The molecular weight and **II** of the cellulose were determined by sedimentation in the ultracentrifuge and by diffusion. The molecular weights calculated from viscosity determinations according to Staudinger gave lower values than those obtained from sedimentation and diffusion. In addition, the fibers were examined by x-rays and the pentosan content, the Cu number, and alkali solubility were determined. Tensile strength and elongation to rupture were found to depend to a large extent on the experimental conditions employed. The resistance to washing of the fibers was studied by boiling in soap solution. A high **I** and low **II** were found to correspond with high strength, low Cu number, and slight alkali solubility. 25 references.

## Double Refraction

**Studies on double refraction of flow. II. The molecular dimensions of zein.** Joseph F. Foster and John T. Edsall. *J. Am. Chem. Soc.* **67**, 617–25 (Apr. 1945).

The relation between the double refraction of a flowing liquid and molecular orientation is discussed. The theoretical use of double refraction data in determination of molecular length is reviewed. A new apparatus providing velocity gradients as high as 30,000 $sec^{-1}$ and the use of high-viscosity solvents such as propylene glycol are described. This apparatus is used to study the relatively short corpuscular protein, zein. Results indicate that zein is a prolate ellipsoidal molecule approximately 300–400 Å. in length. These results agree satisfactorily with sedimentation, diffusion and viscosity measurements of molecular dimensions but not with the results obtained by Elliot and Williams by dielectric dispersion methods.
A. R. Macormac

## Silicones

**The organosilicon polymers.** Eugene G. Rochow. *Chem. and Eng. News* **23**, 612–16 (Apr. 1945).

A brief review of the chemistry, physical properties, and uses of organosilicon compounds and polymers. Unlike common organometallic compounds, organosilicon com-

pounds are not inflammable and the polymers show great stability at high temperatures. The gaseous methylchlorosilanes, which cannot, however, be produced economically at present, exhibit the important property of making cellulosic and certain other surfaces permanently water-repellent. E. F. Evans

## FIBERS: YARNS: FABRICS: MECHANICAL PROCESSES

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### Aralac

**Aralac.** D. G. Carmicheal. *Am. Dyestuff Reptr.* **34**, 171–6 (Apr. 23, 1945).

The history, manufacture, general properties and uses of Aralac are briefly discussed. Proper processing procedure in sizing, desizing, tinting, scouring, dyeing, and finishing is described. Before dyeing, residual acetic acid left in the fiber from the acetylation process (performed to increase hot water, acid and alkali resistance) must be neutralized to prevent too heavy absorption of color by the Aralac; the pH of the dye bath is always an important factor in dyeing this fiber. The use of naphthol and the solubilized vat colors on Aralac-spun rayon mixture appears promising for production of good light and wash-fastness. Dyeing methods for unions of Aralac with spun rayon, wool, acetate, and nylon are discussed; neutral-dyeing acid dyes and chrome dyes found satisfactory in Aralac-wool blends are listed. Aralac is now being produced at the rate of 30,000 pounds per day. C.

### British Empire Cotton

**Empire cotton growing.** Anon. *Text. Mfr.* **71**, 258–9 (June 1945).

Extracts from the report of the administrative council of the British Empire Cotton Growing Corporation. The research policy is discussed as well as present and contemplated projects of the various experimental stations. The transfer of the center of the corporation's scientific work from Trinidad to Uganda is discussed. Other stations will concentrate on the investigation of purely local problems of cotton growing. Results of investigations are discussed in general but no details are given. H. J. Burnham

### Cotton Carding Production

**Cotton carding: production and its effects on quality.** Elliot B. Grover and George H. Dunlap. TEXTILE RESEARCH JOURNAL **15**, 97–162 (Apr. 1945).

In a study of the possibilities for increasing production of cotton cards, various grades of 1 inch and 1⅛ inch cotton were tested and the sliver from each test was spun into yarn—the 1 inch cotton into 20s yarn and the 1⅛ inch into 40s yarn. Complete data were collected for each type of test. Weights, speeds, and machine settings were correctly noted and reported. Power, waste, nep count, and flat-strip weight were tested and recorded. A complete testing routine for all manufacturing processes and conditions was undertaken. This includes fiber-area tests, Shirley analysis, Pressley fiber-strength tests, skein and single-strand strength tests, and yarn appearance tests. The following conclusions were reached: (1) By increasing the overall card speeds, the production may be increased as much as one-third, with a corresponding increase in waste, power consumption, and a drop of not over one-third of a grade in yarn appearance. (2) By increasing the flow of cotton through the card without increasing the cylinder speed—as by increasing doffer speed, sliver weight, or lap weight—the production may be increased over one-half, with reduction in waste, in power consumption per pound of cotton carded, and usually a drop of not more than one-third of a grade in yarn appearance. (3) In either of the above cases there is no significant change in yarn strength. (4) Because increasing card production by raising the speed of the entire card involves increased mechanical deterioration, reduces the power efficiency, and causes increased waste, none of which is encountered under the conditions outlined in conclusion 2, and because the yarn quality characteristics are affected approximately the same way in both cases, it would seem that the method outlined in conclusion 2 is preferable. However, with low grades of cotton, or when higher waste removal is desirable, a combination of the two methods outlined in the first two conclusions might prove advantageous. (5) There is a direct relationship between the speeds of the cleaning members of the card—lickerin, cylinder, and flats—and the amount of waste produced by each. Thus, the overall waste percentage at the card can be controlled within practical operating limits by the regulation of the speeds of these parts. (6) Peak power demand charges should not be increased as a result of using high overall card speeds, as represented by cylinder speeds of 225 r.p.m. for group or line drives. Special problems will exist with individual card drives, which must be met according to the particular conditions of each mill. J.

### Cotton Hose Tests

**Distensibility and bursting strength of cotton hose of various constructions.** Margaret S. Furry and Arnold M. Hansen. *Rayon Text. Mo.* **26**, 173–6 (Apr. 1945).

A report on tests made by the Bureau of Human Nutrition and Home Economics on the behavior of stockings knit in different constructions using both combed and carded single yarns and the corresponding 2-ply yarns. Stockings knit from 80/2 and 40/1 yarns are reported to have given better results with the former showing up a little better. A thorough discussion of test procedures is given, as well as tables of results. H. J. Burnham

### Cotton Substitute in Jap-Controlled Indies

**In Jap-controlled Indies, clothing from ramie and from banana and pineapple.** Anon. *Indian Text. J.* **55**, 408 (Mar. 1945) (from *Foreign Commerce Monthly*).

Jap-sponsored broadcasts report harvesting first crop of ramie in the

Netherlands Indies, where experiments are in progress to replace the dwindling supplies of cotton. In southern Borneo, leaves of banana trees and pineapples are being converted into clothing materials. The spinning mill is said to be under the direction of a Tokyo raw-cotton company. R. K. Worner

## Elasticity

**Elasticity of keratin fibers. II. Influence of temperature.** Henry B. Bull. *J. Am. Chem. Soc.* **67**, 533–6 (Apr. 1945).

A strand of approximately 20 human hairs which had been extracted with ether and alcohol and electrodialyzed was stretched to 2, 5, 8, 15, 25, and 35 percent extension in a water bath at 60° C. The stress decayed at an increasing rate and in about 2 hours had become very small. The temperature was then lowered by definite steps to 17° C. The adjustment of the stress to a change in temperature was very rapid. Another strand was stretched to 25 percent extension at 60° C and allowed to come to approximate equilibrium. It was then allowed to contract to 20, 15, 8, and 4 percent extension and the temperature dependence of stress measured. Stresses are reported in kg./sq. cm. The four-fifth time of stress of a single hair at 25° C was determined up to 40% extension. The relative value of the entropy term and the stress due to internal energy is discussed. It was found that the force of contraction due to internal energy is very much larger than that due to the entropy change. It was concluded that the elastic element of hair involves principally the internal energy, which is in sharp contrast to the condition in rubber. A. R. Macormac

## Mechanism of Felting

**Mechanism of felting of wool fibers.** L. Bohm. *Nature* **155**, 547–8 (May 5, 1945).

Evidence is presented to show that the felting of wool fibers under the repeated application of pressure is not due to local extension and contraction of the fibers but is caused rather by the fiber scales producing a greater friction when rubbed from tip to root than from root to tip. This results in migration of the fibers in the direction of their root ends and causes the shrinkage observed in aqueous media. A correlation was found between the directional frictional effect and degree of felting of different samples. H. W. Theller

## Cattail Fibers

**Swamp cattail joins commercial fibers.** Peter S. Gilchrist. *Textile Bulletin* **68**, 21–2 (July 15, 1945).

A description of the development of the commercial use of fibers from the common cattail, known technically as Typha. The plant has a spike which contains over 100,000 small seeds and several million fibers packed in a close, orderly arrangement. Fibers are less than a half-inch long and occur in clusters of 36. The raw spikes are broken up by a hammer type of disintegrator and the stems, leaves, pollen and other trash separated from the seeds and fibers by passing through a baffle chamber in a current of air. Seeds are separated from fibers by means of a series of chambers and air filters. Typha fiber has been found to be very adaptable for use as a filler in life preservers, beach balls, ring buoys, and buoyant cushions because of its remarkable buoyancy. It is said that a cushion filled with Typha will support 20 times its own weight in water for 265 days. Thermal and sound-insulating properties are also said to be excellent. Some future is predicted for this fiber in blends with wool, cotton, and rayon. The chemical content is 3.85% ether extract (fat and cutin), 0.46% ash, 19.16% lignin, and 76.53% cellulose and hemicellulose. H. J. Burnham

## History of Synthetic Fibers

**Synthetic fibers set the formula for a textile revolution.** Anon. *Chem. and Met. Eng.* **52**, 119–26 (Jan. 1945).

A brief history and the most recent applications of textile fibers from the following raw materials are given: viscose, cuprammonium, cellulose acetate, ethyl cellulose, cellulose acetate butyrate, nylon, vinyl polymer, vinylidene polymer, milk casein, glass, synthetic rubber, polyethylene, polystyrene, soy-bean protein, cornmeal zein, aluminum, peanut protein, sodium alginate, California redwood fiber, and plastic-coated yarns. Tables showing the comparative tensile strength and elongation and listing manufacturers of these fibers are presented. E. D. Klug

## Properties of Synthetic Fibers

**Properties of synthetic fibers.** Wm. D. Appel. *Modern Plastics* **22**, 155–8, 194 (May 1945).

The properties of a number of synthetic fibers are compiled in 10 tables, namely: (1) composition and structure, (2) dimensions and configurations, (3) tensile strength, (4) extensibility, (5) recovery on unloading, (6) modulus of elasticity, (7) relative stiffness, (8) relative toughness, (9) density, and (10) effect of temperature. E. G. Martin

## Yucca Fibers

**Tensile strength of yucca fibers.** C. W. Botkin and L. B. Shires. *N. Mex. Agr. Expt. Sta., Tech. Bull.* **316**, 30 pp. (1944); cf. *C.A.* **38**, 3480[7] (through *Chem. Abstr.* **39**, 2882[4] (July 10, 1945)).

The average tensile strengths in km. from the following species of yucca were: *Y. glauca*, 44.7; *Y. elata*, 47.5; *Y. baccata*, 60.2; *Y. torreyi*, 61.1; *Y. schidigera*, 50.4, and *Y. faxoniana*, 54.0. Autoclaving at high temperature, the use of $Na_2CO_2$ and Na and Ca bisulfites at concentrations and temperature high enough to soften the leaves reduced the strength of the yucca fibers. Flexible-leaved yuccas such as *Y. glauca* and *Y. elata* were harmed by cooking above 25 pounds steam pressure for more than 1 hour. Bayonet-type leaved yuccas such as *Y. baccata*, *Y. torreyi*, *Y. schidigera*, and *Y. faxoniana* required at least 25 pounds of pressure for 1 hour; above 40 pounds deterioration of the fiber occurred. The fiber is more easily extracted from

green leaves than from dried leaves. Fiber from flexible-leaved species is finer and softer than fiber from the bayonet-leaved species. Yucca fibers are equal in strength to the usual commercial fibers. Further research on decortication and cleaning of the fiber is required if yucca fiber is to compete with present commercial fibers.

## Fibers and New Developments

**Fibers and new developments.** H. Wickliffe Rose. *Fibre and Fabric* **98**, 14–20, 37–8 (June 30, 1945).

In a paper delivered before the American Association of Textile Technologists, the author briefly outlines some of the research that has been and is being undertaken by individuals and organizations in this country, reviews the direction in which research in fibers and treatments is progressing, and stresses the educational needs of the industry. J.

## Fiber Regain Data

**Fiber regain data simplified.** C. H. Reumann. *Textile World* **95**, 101–3 (June 1945).

An elementary discussion is given of the relation of fiber regain to relative humidity. Charts are included giving: (1) the absolute humidity of the air in grains of water per cubic ft. at any temperature and humidity, (2) relative humidity at any wet bulb depression and dry bulb temperature, and (3) regain of the 6 most important fibers at a given humidity and temperature.

H. J. Burnham

## Rag Stock for Papermaking

**Fibers and chemicals used in present-day fabrics.** H. W. Wilkinson, Jr. *Paper Trade J.* **120**, 37–8 (May 24, 1945).

Because of the consumer demand for more permanent finishes and colors, the textile industry has developed products that are difficult to process when they reach the paper mill. The different classifications of finishes and colors are briefly discussed and the method of treatment for removing them indicated. In some cases, as in fabrics treated with vinylite or synthetic rubbers, more research will be required to reach a satisfactory solution. Author

## Rayolanda

**"Rayolanda"—A Courtaulds product.** Anon. *Text. Mercury and Argus* **112**, 341, 345–6, 348–9, 351 (Mar. 23, 1945).

"Rayolanda" is a chemically modified cellulosic fiber of distinctive properties. Among these are: adaptability to all spinning systems, resilience, full hand, accelerates the milling of wool, excellent for raising and brushing, distinctive dyeing qualities, and moth-proofness. Instructions, including machine settings, are given for processing it on the cotton, woolen, worsted and flax systems, as well as detailed information relative to scouring and dyeing.

A. R. Martin

## Plastics and Rayon Production

**Commodity reviews:** Plastics—Rayon and synthetic fibers. Anon. *Chem. and Met. Eng.* **52**, 136–7 (Feb. 1945).

The most recent data on plastics and rayon production are given. The output of rayon in 1944 was 9.2% greater than ever before. Tire yarns were mainly responsible for the increase. E. D. Klug

## Spinning Wool on Cotton System

**Wool manufacturing on the cotton system.** Anon. *Am. Wool and Cotton Reptr.* **59**, 13, 15 (July 19, 1945).

An article stressing the contention that it is much cheaper to spin woolen and worsted yarns on the cotton system than by the conventional method. Ply yarns are said to be entirely suitable for the manufacture of many fabrics. Wool processing on the cotton system is admitted to be going through an experimental period, but a plea is made for wool growers to institute extensive research to keep wool on a competitive basis with synthetics and blends. H. J. Burnham

## Water-Tight Fabrics

**Water-tight fabrics made by swelling cotton fibers.** Charles F. Goldthwait and Herbert O. Smith. *Textile World* **95**, 105, 107, 196, 198 (July 1945).

An outline of a method developed by the Southern Regional Laboratory for finishing cotton yarn for heavy fabrics such as unlined emergency fire hose, water bags, tents, and tarpaulins whereby a commercial hydroxy ethyl ether of cellulose is precipitated on the yarn. This is soluble in caustic alkali but not in water and reswells on wetting. Large-scale demonstrations have not yet been made. Reference is made to successful attempts by the Shirley Institute to do the same thing by using mercerized cotton yarn. H. J. Burnham

# BLEACHING: DYEING: FINISHING

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## Dyeing Nylon

**Nylon fibre: a study of the mechanism of the dyeing process with acid dyes.** R. H. Peters. *J. Soc. Dyers and Colourists* **61**, 95–100 (Apr. 1945).

It is clearly indicated that the dyeing of nylon with acid dyes takes place in two ways. At normal dye bath pH values—viz., above pH 3—combination of dye with end amino groups occurs. The amount of dye which can combine in this way is strictly limited. At lower pH values combination with the weakly basic amido groups can take place, and the amount of dye which can be bound in this way is very great. The dyeing of nylon fiber differs from the dyeing of wool at normal dye bath acidities merely in the greatly reduced number of basic sites available (about one-sixteenth of those in wool), and in the greater affinity of the dye anions for nylon. This second factor is shown in practical dyeing by the greater fastness of dyes on nylon as compared with wool. The limited number of amino groups in nylon has an important effect on the dyeing of this fiber, for 2–4% of a commercial dye may rep-

resent saturation. Consequently, if mixtures of dye are applied to nylon in reasonable quantity, there may be competition for the available sites and unless the dyes are chosen carefully one dye may exclude another. This effect is also evident at lower dye concentrations, especially in the early stages of dyeing when the dyes compete for the surface of the fiber, from which they diffuse inward. It is difficult to see how such competition can be eliminated except by the selection of dyes having exactly the same affinity for nylon, or by the preparation of new polyamides containing a greater number of amino groups.

Author

**The dyeing of nylon with direct cotton dyes in the presence of cationic soaps.** J. H. MacGregor and C. Pugh. *J. Soc. Dyers and Colourists* **61**, 122–5 (May 1945).

In the dyeing of nylon with direct dyes in an acid bath the inclusion of cationic paraffin-chain salts increases the rate of dyeing when they are present in quantities of less than 1% of the weight of the nylon. When present in the acid dye bath to the extent of 5% or more, dyeing of the nylon is inhibited. These phenomena depend upon the number of carbon atoms in the hydrocarbon chain in the cation of the salt. Very short-chain salts, whether formed from a strong or a weak base, behave as neutral inorganic salts—i.e., they decrease the rate of absorption of the dye. The increase in the rate of dye absorption begins to be appreciable when the hydrocarbon-chain cation contains about 8 carbon atoms and is fully evident in the dodecyl and hexadecyl salts. The addition of small quantities of such salts is of particular value when used to decrease the time required to exhaust very slow-dyeing direct cotton dyes on nylon from an acid bath.

Author

## Phthalocyanine Dyes

**Phthalocyanine colouring matters—their chemistry and uses.** N. H. Haddock. *J. Soc. Dyers and Colourists* **61**, 68–73 (Mar. 1945).

The discovery of the new chromogen phthalocyanine occurred in 1928 as a result of investigation of a blue impurity in technical phthalimide. Most metallic salts react with phthalonitrile, and metallic phthalocyanines have been synthesized from representative metals in every group in the Periodic Table. They are generally characterized by water insolubility, and a number possess high chemical stability. The variation in degree of stability may be accounted for by the structure assigned to the phthalocyanines which postulates the attachment of hydrogen or metal to two of the isoindole nitrogen atoms by primary valencies (covalencies or electrovalencies), and coordination with the other two isoindole nitrogen atoms to form chelate rings. Electrovalent linkages give rise to compounds of superior solvent insolubility, whereas covalent linkages, if the metals concerned are of atomic radii which fit reasonably well into the center of the phthalocyanine molecule, completely resist the action of acids. Phthalocyanine itself is a perfect example of resonance, to which is attributed its high stability and tinctorial value. The preparation of metal-free phthalocyanine, and a variety of metallic and nuclear substituted phthalocyanines is described. The brightness, tinctorial power, and lightfastness of these pigments makes them valuable in the manufacture of inks and paints, and in the coloration of plastics, paper, and textiles. The color range of the metallic phthalocyanines is from blue to green; the copper derivative being reddest and lead greenest. Technically, all the shades required are provided by copper phthalocyanine (Monastral Fast Blue B), phthalocyanine itself (Monastral Fast Blue G), and highly chlorinated copper phthalocyanine (Monastral Fast Green G). C.

## Permanent Finishes

**New developments in permanent cellulose finishes.** S. M. Edelstein. *Am. Dyestuff Reptr.* **34**, P136–9 (Mar. 26, 1945).

The preparations, properties, and applications of so-called catalytically activated caustic solutions of cellulose are described. The preparation is based on the solvent power for cellulose possessed by 8–10% sodium hydroxide solution at temperatures under 40°F when zinc or any one of certain related elements is added. Solutions prepared in this way are commercially available containing 5–7% cellulose; the solution may be applied to fabrics by padding and the cellulose may be precipitated on the goods by a treatment in an acid solution, salt solution, caustic of mercerizing strength, or by drying at above 160°F. Finishing consists of neutralizing or rinsing to remove alkali. This type of finish may be applied at any desired stage of processing as it is unaffected by kier boiling, bleaching, or dyeing; it may be utilized to give a variety of hand effects, shrinkage control, yarn slippage control, and as a binding medium in pigment dyeing. An interesting development is its use in vat-dyeing spun rayon fabrics; the vat pigments are dispersed in the cellulose solution and the fabric is padded through this solution. The cellulose is coagulated with acid and, after rinsing, the goods are passed through the usual reducing bath and finished in the normal manner; advantages claimed are negligible loss of color in the reduction bath, lofty hand of the goods, thorough penetration, and shrinkage controlled permanently at less than 2%. C.

## Resin Finishing

**What we may expect from resins in the treatment of cotton.** D. H. Powers. *Am. Dyestuff Reptr.* **34**, P191–3 (May 7, 1945).

The potentialities of resin treatments in creating new markets for cotton through improved strength (by increasing friction of fiber surfaces in yarns, thus utilizing more of the potential strength of the fiber), improved resilience, abrasion, water, and mildew resistance, and other types of durable finishes, are discussed. C.

## Mildewproofing

**Report of AATCC cooperative tests for determining mildew- and rot-resistance.** Sub-Committee on Mildewproofing. *Am. Dyestuf*

*Reptr.* **34**, P128–35, 139–40 (Mar. 26, 1945).

A summary of the results obtained by 12 laboratories participating in the program investigating rot-resistance test methods is presented. Six microbiological tests were performed on a standard fabric treated with 5 graduated dosages of 3 commercial fabric fungicides (copper naphthenate, dihydroxydichlorodiphenylmethane, and phenylmercury triethanol ammonium lactate). The greatest variations in test results occurred in the case of samples having the lower concentrations of fungicides; at concentrations approaching those at which effective protection is afforded a fairly consistent relationship is shown between concentration of treatment and percent of fabric strength retained. Although in the absence of actual service test data it is difficult to make an overall evaluation of the resistance of the different fungicides on the basis of any one of these tests, it would appear possible to arrive at a practical evaluation by the use of a combination of two tests using pure cultures and one soil contact test. A detailed description of all the test methods employed is included. C.

## Phthalocyanine Dyes

**Some green pigments of the phthalocyanine series.** J. W. Haworth, I. M. Heilbron, D. H. Hey, R. Wilkinson, and E. F. Bradbrook. *J. Chem. Soc.* **1945**, 409–12 (June 1945).

A number of tetraphenylphthalocyanines and tetrapyridylphthalocyanines and their copper derivatives have been prepared by standard methods from the corresponding phenyl- or pyridyl-phthalonitriles or phthalic acids. The preparation of various other intermediates for tetrapyridylphthalocyanine is also described. Both tetraphenyl- and tetrapyridylphthalocyanine are bright green pigments; the latter possesses basic properties and gives rise to water-soluble quaternary salts, which show direct affinity for cotton and viscose rayon and are fast to washing and light.

E. F. Evans

## Wool Dyeing

**Two-color dyeing of all-wool materials.** F. Townend. *J. Soc. Dyers and Colourists* **61**, 144–9 (June, 1945).

The difference in the dyeing properties of chlorinated wool and normal wool may be utilized to produce contrasting tone-in-tone effects on unions of these two materials. Investigation has shown that the use of selected "crystalloidal" dyes in the presence of certain retarding agents will give a result far superior to that previously obtainable. The retarding agents (e.g., Tanninol WR, a complex phenol-sulfur condensate) act by retarding the rate of dyeing of normal wool to a greater extent than for the chlorinated wool and by altering the final dye-wool equilibrium; they operate presumably by competing with the dye for the wool. The contrast producible with level dyeing acid dyes depends on the number of sulfonic acid groups per molecule, being greatest when more than two such groups are present. Dyes fast to wet processing have an advantage over the level dyeing acid dyes in that the contrast initially achieved is not appreciably lost in the boiling dye bath; the dyeing of chrome-mordanted material is best in this respect. Mixtures of dyes used must be compatible in that they must give tone-in-tone rather than off-tone effects in the finished material. C.

## Processing Nylon

**Some aspects of processing nylon yarns, and the setting and finishing of nylon fabrics.** G. Loasby. *J. Soc. Dyers and Colourists* **61**, 64–8 (Mar. 1945).

The historical development, the physical and chemical properties of nylon yarn, and proper technique in handling nylon through the processes of coning, oiling, throwing, knitting, sizing, warping, weaving, setting, and finishing are reviewed in some detail. A list of patent specifications relating to the treatment and finishing of nylon yarns and fabrics is presented. C.

## Rotproofing Fabrics with Copper

**Dimethylglyoxime-Cu treatment for rotproofing fabrics.** A. C. Neish, G. A. Ledingham, and A. G. Mackey. *Can. J. Research* **23F**, 198–201 (1945) (through *Chem. Abstr.* **39**, 3437[2] (Aug. 10, 1945)).

Jute, coarse cotton, and woolen fabrics were dipped for 2–5 min. in a 0.5% aqueous solution of dimethylglyoxime at 90–100°, and then immersed in 5% $Cu(OAc)_2$ at room temperature for 5 min. The amount of fixed Cu was varied by altering the strength of the Cu solution. The treated fabrics were odorless, remained pliable, and were dyed a khaki color. This treatment was more effective than that with Cu naphthenate for rotproofing the fabric.

# MISCELLANEOUS

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## Castor-Bean Proteins

**Preparation of castor-bean proteins.** M. S. Tartakovskii and V. D. Matveev. *J. Applied Chem.* (U.S.S.R.) **17**, 274-81 (1944) (English summary) (through *Chem. Abstr.* **39**, 3176[6] (July 20, 1945)).

Proteins suitable for the manufacture of staple fiber or of plastic masses can be obtained from both oil-cake and coarsely ground castor beans. Yellow protein is obtained if the beans are preheated and steamed; white protein, from beans not subjected to heat. Oil-cake and ground beans readily yield the protein by treatment with 10% NaCl at 50°, followed by filtration and acidification.

## Dielectric Heating

**Principal limitations of dielectric heating.** Carl J. Madsen. *Plastics and Resins*, **4**, 11–14 (Mar. 1945).

Dielectric heating costs approximately $0.025 to $0.04 per KWH; it is applicable only to materials normally considered poor electrical con-

ductors. The dimensions, including thickness, shape, and area of the dielectric material used, the frequency and total voltage permissible between electrodes, voltage gradient, loss due to materials absorbing energy, and the transfer of heat to the electrodes all may be limiting factors in dielectric heating.

E. G. Martin

## Electron Microscopy

**A bibliography of electron microscopy. III.** Claire Morton and Samuel Sass. *J. Applied Physics* **16**, 373–8 (July 1945); cf. **I**, TEXTILE RESEARCH **14**, 63 (Feb. 1944); **II**, **14**, 344 (Oct. 1944).

This brings up to date the bibliography previously published in Parts I and II.

## Industrial Fire Risks

**Industrial fire risks.** W. F. Cooper and F. H. Mann. *J. Inst. Elec. Engrs.* (London) **91**, 267–85 (1944) (through *Chem. Abstr.* **39**, 3431[9] (Aug. 10, 1945)).

A complete and comprehensive exposition is given in Part I covering fire-resisting materials, fireproof buildings, and the contents of buildings. Useful tables of flash points of inflammable industrial solvents, spontaneous ignition temperature, and limits of inflammability of a number of substances are included. Other topics discussed are spontaneous combustion, dusts, electric equipment, insulating oils, cables, earth leakage, and flame-proof construction. Part II deals with specific hazards in, e.g., gas works, oil-refining, hydrogenation, and textile industries, and suggests measures for their reduction. A bibliography and report of subsequent discussion are given.

## Evaluation of Flaxseed

**Detection of fraud in the purchase and sale of flaxseed for fiber production.** Manuel Rodríguez Escribens. *Actas y trabajos congr. peruano quím.* **2**, **I**, 406–8 (1943) (through *Chem. Abstr.* **39**, 3671[8] (Aug. 20, 1945)).

Flaxseed for fiber production (I) generally contains oil less than 30% and moisture 10–12%; the seed for oil production (II) contains 42% or more of oil when ripe. Green I may be used to adulterate II; all samples containing an appreciable quantity of dark-greenish seeds should be rejected. A yellow-to-greenish color of the oil indicates the presence of II. The iodine numbers and refractive indexes of the oil are found somewhat lower for I than for II.

## University of Leeds

**Textile industries at the University of Leeds.** Anon. *Nature* **155**, 73 (Jan. 20, 1945).

Descriptive. H. W. Theller

## Margins in Manufacturing and Marketing Textiles

**Marketing and manufacturing margins for textiles.** L. D. Howell. U. S. Department of Agriculture Technical Bulletin No. 891. Washington, Government Printing Office, March, 1945. 148 pages. Price, $0.20.

This report is part of a broader analysis of marketing margins and costs by the Bureau of Agricultural Economics, and deals with the breakdown of price spreads between the farmer and the ultimate consumer and the possibility of reducing them. Costs and charges for marketing raw cotton and raw wool, manufacturing them into cloth and knit goods, dyeing and finishing them, converting them into apparel and household goods, and wholesaling and retailing these products, are comprehensively analyzed on the basis of data obtained from the Office of Price Administration, Federal Trade Commission, and other public and private agencies. It is stated that in 1939 only 7.5¢ of the consumer's dollar paid for cotton clothing and household goods went to farmers, and less than 3¢ of the dollar for ginning, baling, and delivering the raw cotton to the mills. Spinning and weaving cost 10.5¢ of the consumer's dollar; dyeing and finishing, 8.5¢; converting the cloth into clothing and household goods, 29.9¢; wholesaling, 8.2¢; and retailing, 32.6¢. Analyzed from another viewpoint, about 48¢ of the dollar paid by the consumer in 1939 for apparel and household goods made of cotton went to non-farm salaries and wages, 4.2¢ to advertising, 8.5¢ to non-farm profits, 3.2¢ for other non-farm costs, and 7.5¢ for farm production charges including hauling of cotton to the gin. A similar analysis for apparel and household goods made of wool indicated that 11.4¢ of the consumer's 1939 dollar went to the farmer, 2.7¢ for marketing the raw wool, 13.4¢ for manufacturing, dyeing, and finishing, 34.6¢ for converting into consumers' goods, 3.1¢ for wholesaling, and 34.8¢ for retailing. Wherever possible, comprehensive data are presented regarding costs and charges for the various steps involved in manufacturing and marketing textiles. R. B. Evans

## Rayon Labor Productivity

**Rayon labor productivity.** Anon. *Rayon Organon* **16**, 105–9 (July 1945).

Rayon filament yarn production, in terms of pounds, increased 16% from 1942 to 1944, entirely due to a four-fold increase in the production of heavy denier tire yarn. But if these poundages are adjusted to a constant denier, it is found that the yardage of rayon produced has actually declined 3% from 1942 to 1944. Total rayon yardage output per man-hour worked reached a peak in 1942, but by 1944 it had declined by 12% or to the 1941 level. With this decline in labor productivity, plus higher hourly wage rates due to increase in basic rates as well as overtime and other premium rates, the unit labor cost rose substantially. Thus from 1941 to 1944 the unit labor cost of rayon production increased by 24%. It is shown that labor hours expended in yarn production are essentially proportional to the linear yards of rayon spun; also that the labor expended per pound of rayon spun is inversely proportional to the denier of the yarn spun. Production totals from 1939 to 1944 are compared. Rayon output per man-hour and unit labor cost for the period are illustrated by a chart. J.

## Plastics

**Developments in plastics for textile applications.** Anon. *Am. Wool and Cotton Reptr.* **59**, 11–12 (Aug. 30, 1945).

A discussion of the possibilities of plastic sheeting replacing woven fabrics as decoration materials, awning fabrics, and the like when lack of porosity is not a factor. It is predicted that length and satisfaction of service will outweigh higher cost.
H. J. Burnham

## Abrasion Resistance of Plastics

**Wear and abrasion resistance of plastics.** Don Masson. *Plastics and Resins* **4**, 9–11 (Apr. 1945).

A résumé of results of field tests on the wear and abrasion resistance of plastics. Included are: phenolic molding material, laminates, coatings, electrical insulations, and vinyl plastic sheeting. E. G. Martin

## Polythene

**Polythene: physical, and chemical properties.** F. C. Hahn, M. L. Macht, and D. A. Fletcher. *Ind. Eng. Chem.* **37**, 526–33 (June 1945).

The hydrocarbon resin, polythene, recently became available commercially from domestic sources. The low electrical losses, along with high resistance to moisture and chemicals and toughness over a wide range of temperatures, have lead to its wide usage, particularly in the electrical field. These properties indicate other potential applications. The unusual resistance of this material to various chemicals suggests other fields for its use. Data show the effects of exposure to various chemicals on the physical properties. They point to such applications as special types of equipment—containers, gaskets, tubing, etc. As a means of protecting metal surfaces from corrosion and applying polythene coatings in general, the process of flame-spraying the powdered material is described. Certain flame-sprayed compositions show good adhesion to metals, and give excellent protection against corrosion by water, brine, etc. Data are presented on other physical properties of polythene, such as the relation of density or volume to temperature.
Author

## Protein Bristles

**Artificial bristles from proteins.** T. L. McMeekin, T. S. Reid, R. C. Warner, and R. W. Jackson. *Ind. Eng. Chem.* **37**, 685–8 (July 1945).

A 30% aqueous solution of commercial casein (9% water) at 95°C is extruded through a die with holes 0.3–0.6 mm. diameter into a solution containing 2% formaldehyde, 0.1% naphthalene sulfonate, and 10% sodium sulfate with a pH of 4.7. The fibers are collected on a reel. Skeins from this reel are stretched at the rate of 1% per minute while immersed in a saturated quinone solution at room temperature until approximately 100% extension is obtained. The fiber should remain under tension in this bath for 24 hrs. Further hardening and reduction of water absorption may be obtained by an additional 24-hr. soaking in 2% formaldehyde under tension. Such fibers have a dry strength of 0.7–0.8 grams per denier. Their wet strength is about one-half the dry strength. Bristles cannot be set in brushes by vulcanization of rubber because they will not stand temperatures over 100°C, but urea formaldehyde or alkyd resins may be used. The brushes are resistant to oils and fat solvents but soften when allowed to stand in water. They have good paint-carrying ability, make smooth films, and have good wear resistance. Quinone is superior to formaldehyde as a hardening agent. A. R. Macormac

## Rayon Production and Consumption Data

**World rayon production and consumption.** J. Guthrie Oliver. *Silk and Rayon* **19**, 251, 253 (Mar. 1945).

A brief discussion is presented on world rayon production and consumption, including post-war demands, consumption before the war, industrial usage, new developments in rayon, and the effect of the war on the fabric trade. Tables show the world consumption of textiles in the pre-war period for clothing, household goods, and industrial uses.
A. L. Merrifield

## Sericulture

**Treatment of silkworm eggs—some practical suggestions.** V. M. Appadhorai Mudaliar. *Indian Text. J.* **55**, 240–1 (Jan. 1945).

Careful, intelligent handling of the eggs from the time they are laid until they are hatched is necessary.
R. K. Worner

## Sulfonated Castor Oil

**Industrial application of sulfonated oils to textiles and leather.** Carlos José Ratto. *Actas y trabajos congr. peruano quím.* **2**, I, 391–3 (1943) (through *Chem. Abstr.* **39**, 3681[8] (Aug. 20, 1945)).

A discussion of the developments in this industry with reference to Peru. The preparation of castor oil and sulfonated castor oil is described in detail.

## Synthetic Fibers

**This month's progress in rayon and synthetic fibers.** Anon. *Silk and Rayon* **19**, 193–6 (Feb. 1945).

A brief discussion is given of the following subjects: (1) some recent manufacturing developments in cellulose ester rayons; (2) an apparatus for hardening casein fibers (B.P. 565,011); (3) the analysis of the alpha-amino acids tryptophane and tyrosine in proteins; (4) use of casein fibers (B.P. 564,141) and soya bean fibers (B.P. 565,187) in the manufacture of felt hats; (5) modifying the extensibility of nylon yarns by treatment with formaldehyde (B.P. 534,698 and 565,066); and (6) production of nylon fibers with improved dyeing properties (B.P. 565,350). A. L. Merrifield

**This month's progress in rayon and synthetic fibers.** Anon. *Silk and Rayon* **19**, 309, 311, 313, 329 (Mar. 1945).

A brief discussion is given of the following subjects: (1) pretreatment

before acetylation of cotton linters for acetate rayon with organic acid of low molecular weight, such as formic acid (B.P. 565,812); (2) selective saponification of acetate rayon for embossing (B.P. 565,731); (3) new dyes for acetate rayon of the mono-azo type (B.P. 565,697); (4) production of vinylchloride (B.P. 566,003); (5) investigation of the possibility of acetylating casein fibers to improve wet strength and other properties; (6) the removal of casein from milk by super-centrifuging; and (7) solutions of polyamides in an aliphatic alcohol containing a suitable inorganic salt such as calcium chloride (B.P. 563,078). A. L. Merrifield

## Transformers

**Electrical plant—high voltage step-down transformers.** Anon. *Silk and Rayon* **19**, 332–3, 340 (Mar. 1945).

A general review of the construction, use, and maintenance of high-voltage step-down transformers, including tapping the secondary winding for various voltages, effect of current lag on voltage, oil-cooled windings, and determination of power output, with diagrams showing the connections of Delta-Star step-down transformer and a method of on-load transformer tap-changing, is presented. A set of curves give the efficiencies of various transformer designs having the same total loss at full load. A. L. Merrifield

## Wages in Textile Industry

**Earnings in the textile industries** (United Kingdom). *Text. Recorder* **62**, 40–2 (May 1945); 36–8, 49 (June 1945).

Earnings of men employed in the textile industries of the United Kingdom averaged 2.0 shillings per hour and 101 shillings and 10 pence per week in July, 1944, increases of 66% and 78%, respectively, over earnings in October, 1938. The textile industries paid the lowest weekly wages to men of England's 16 industry groups in 1938, but ranked third from the lowest in 1944. Similar data are given for youths and boys, women, and girls. In the June issue, data on hours worked and on hourly and weekly earnings are given for each of 11 major branches of the textile industry, including cotton, woolen and worsted, rayon, etc., for the period from 1938 through 1944. R. B. Evans

## Wood Pulp

**Wood pulp for rayon production.** A. G. Arend. *Silk J. Rayon World* **21**, 31–2, 38 (June 1945).

Modern methods for handling the original logs and for converting them into pulp are described. R. K. Worner

## Worsted Tops

**Manufacture of worsted tops at Arlington Mills.** Anon. *Cotton* **109**, 91–4 (July 1945).

An elementary description of the commercial manufacture of worsted tops of interest to the cotton mill man unfamiliar with worsted mill practice who might be contemplating the running of worsted on the cotton system. H. J. Burnham

## British Research Fellowships

**£ 35,000 for Education and Research.** Anon. *The Dyer* **93**, 507–8, 528 (June 22, 1945).

A plan for research fellowships has been established by Textile Machinery Makers, Ltd., for the furtherance of higher education and research in relation to the textile industries. The plan provides for the expenditure of £ 35,000 over a period of seven years. Provision is made for undergraduate as well as postgraduate scholarships and research fellowships. Courses to be followed will be in textile engineering, mechanical engineering, textile technology, or economics. The normal tenure of a postgraduate scholarship will be three years; in groups I and III of the undergraduate scholarships, three years, and group II, four years. During the first year of the operation, the following awards will be offered:

| *Scholarships* | *Group* | *Number* |
|---|---|---|
| Undergraduate | I | Five |
| Undergraduate | II | Three |
| Undergraduate | III | Two |
| Postgraduate | IV | One |

The value of these awards ranges from £ 250 to £ 550 per year. J.

**Scholarships and research fellowships in the textile industries.** Anon. *Nature* **155**, 750–1 (June 23, 1945).

Describes the scholarships and fellowships established by certain British textile machinery manufacturers to further higher education and research in relation to the textile industries. H. W. Theller

## PATENT REFERENCES

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## Improved Bobbin Magazine

**Bobbin magazine for weft replenishing looms.** Clifford Darwin (to Crompton & Knowles Loom Works). U. S. 2,381,725 (Aug. 7, 1945).

An improved type of bobbin magazine for weft replenishing looms is described. The usual slotted end plate which must be supported by means of a number of tie rods is replaced by a solid end plate. To replace the slots as a means of guiding the weft ends of the reserve bobbins a series of guide wires extend along the outer sides of the plate. A. R. Martin

**Bobbin magazine for weft replenishing looms.** Richard G. Turner (to Crompton & Knowles Loom Works). U. S. 2,381,790 (Aug. 7, 1945).

This invention relates to a weft replenishing mechanism which is capable of operating with stacks of bobbins having different butt diameters or with stacks of bobbins the yarn diameter of which is less than the butt diameter. This result is accomplished by means of adjustable guideways for the bobbins. A. R. Martin

## Bobbin Lifting Apparatus

**Bobbin lifting apparatus.** Clarence Mr. Asbill, Jr. (to Monarch Mills). U. S. 2,381,482 (Aug. 7, 1945).

An attachment for spinning frames consisting essentially of a plurality

of lifting fingers, one for each spindle, caused to push up on the bottom of each bobbin by means of a pipe extending the length of one side of the frame when turned by means of a handle on one end, thus releasing every bobbin on that side from its grip on the spindle for ease in doffing. H. J. Burnham

## Drafting Mechanism

**Drafting mechanism for textile fibers.** Joseph Noguera (to Casablancas High Draft Co., Ltd.). U. S. 2,381,983 (Aug. 14, 1945).

This invention relates to drafting mechanisms for textile fibers of the type using endless belts engaging and guiding the fiber being drawn. According to the present invention, the endless belts are so arranged with respect to the front drawing rollers that the flattened strand of fibers passes from between the endless belts and is delivered to the front drawing rollers in a plane at right angles to the line of contact of the drawing rollers, while the surfaces of the belts which are gripped between the belt driving rollers are in a plane at right angles to the plane in which the strand passes from between the belts.

## Knitting Machine

**Improved full-fashioned type of knitting machine.** Kenneth Howie and Charles C. Krieble (to Wildman Mfg. Co.). U. S. 2,379,527 (July 3, 1945).

This invention relates to knitting machines of the full-fashioned type, and more particularly to a mechanism therefor for turning the welt of a lady's full-fashioned hose knit on such a machine. With the mechanism of this invention, the yarn of the initial course of the fabric is automatically caught upon points, and these points subsequently automatically deliver the loops of that initial course to the needles in order to close the welt. Furthermore, after the loops of the initial course of the fabric have been delivered to the needles, the points are automatically removed to an active position so that knitting of the remainder of the fabric will proceed without interruption.

## Looms

**Harness mechanism for looms.** Oscar V. Payne (to Crompton & Knowles Loom Works). U. S. 2,379,742 (July 3, 1945).

Object of the invention is to provide means by which the bearings for the harness connector sheaves may be wide enough to resist objectionable wear.

**Improved harness cord sheave mechanism for looms.** Oscar V. Payne (to Crompton & Knowles Loom Works). U. S. 2,379,743 (July 3, 1945).

**Selector mechanism for multistack weft replenishing looms.** Wilfred C. Howe (to Crompton & Knowles Loom Works). U. S. 2,379,487 (July 3, 1945).

This invention relates to improvements in weft replenishing looms having a pair of stacks of reserve bobbins for each of two shuttles. It is the general object of the invention to provide means for drawing bobbins alternately from either pair of stacks during the succession of replenishing operations involving the shuttle corresponding thereto.

## Axminster Looms

**Adjustable tuft cutting knife for Axminster looms.** Albert Palmer (to Crompton & Knowles, Loom Works). U. S. 2,379,740 (July 3, 1945).

## Wool Sampler

**Improvement in wool sampling.** Alexander Johnston and George C. Le Compte (to U. S. Dept. of Agriculture). U. S. 2,378,484 (June 19, 1945).

A coring device for sampling loose wool in bags or bales. It is said to overcome previous deficiencies in this type of device and yields samples more truly representative.

## Picker Stick

**Picker stick guide.** Edward C. Nichols (to Draper Corp.). U. S. 2,379,589 (July 3, 1945).

Improved picker stick guide for automatic looms.

## Thread Advancing Device

**Method and apparatus for handling filamentary material.** Alexander Bruenner (to American Viscose Corp.) U. S. 2,381,643 (Aug. 7, 1945).

A thread advancing device is disclosed which is particularly adaptable for use in staple rayon manufacture. It is claimed that this device overcomes the difficulties encountered in lacing up the tow from a spinning machine to the cutter.

A. R. Martin

## Automatic Threading Shuttle

**Automatic threading shuttle.** Edward C. Nichols (to Draper Corp.). U. S. 2,379,650 (July 3, 1945).

Invention relates particularly to a means for maintaining uniform tension on the filling thread as it runs through the shuttle.

## Yarn Friction

**Device for measuring yarn friction.** Charles Thomas Zahn (to American Viscose Corp.). U. S. 2,378,614 (June 19, 1945).

The invention relates to apparatus for measuring the yarn friction with respect to metal or other surfaces and particularly for determining the frictional characteristics of yarns finished with lubricating, sizing, twist setting, or other compounds, in order to evaluate the effectiveness of such compounds.

## Photoelectric Recording

**An improved photoelectric controlling or recording apparatus.** Robert L. Hood (to American Cyanamid Co.). U. S. 2,379,233 (June 26, 1945).

Essentially, the novelty of the present invention lies in the use of flickering light and in the type of ampli-

fier. The features of the invention can be used in a wide variety of devices which require the following of a light beam without materially altering the constituent parts of such devices. This general applicability of the amplifier and phototube of the present invention constitutes an important practical advantage, as it can readily be added to existing devices without major reconstruction.

## Flickering-Beam Spectrophotometer

**Spectrophotometer.** Orrin Weston Pineo (to American Cyanamid Co.). U. S. 2,383,075 (Aug. 21, 1945).

This invention relates to amplifiers for photoelectric and similar inputs from spectrophotometers, which inputs contain spurious signals at a higher frequency than the signal to be amplified, and more particularly to such amplifiers provided with rejector circuits for said spurious signals. The present invention is primarily useful in the amplifiers for flickering-beam spectrophotometers such as those described in prior Patents 2,107,836 and 2,126,410.

## Casein Fibers

**Treatment of casein or the like protein fibers.** Robert Louis Wormell (to Courtaulds Ltd.). U. S. 2,383,358 (Aug. 21, 1945).

This invention relates to the hardening or other treatment of a continuous tow of "casein or the like protein fiber." The tow is fed in convolutions onto the surface of a hardening liquid of specific gravity greater than the specific gravity of the fibers, so that the convolutions of the tow float on or in the treating liquid, allowing the tow to accumulate in the liquid for sufficient time to produce the desired effect and thereafter continuously withdrawing the tow from the treating liquid at a rate substantially equal to the rate of feed by removing the tow from the underside of the mass of convolutions and then conducting the tow out of the liquid through guiding means so that entanglement of the tow is avoided.

## Chlorination of Bast Fibers

**Apparatus for the chlorination of bast fibers.** Helmuth Korte, Wilhelm Waibel, and Johann Metzger (vested in Alien Property Custodian). U. S. 2,382,726 (Aug. 14, 1945).

An improved method for the chlorination of piece goods from vegetable, animal, and artificial fibers is described. The process consists of impregnating the goods in an impregnating apparatus with freshly prepared, supersaturated chlorine water and by continuously compensating the chlorine consumed by introduction of chlorine gas. For this purpose the apparatus for the preparation of the chlorine water is preferably constructed in such a manner that it yields strongly supersaturated chlorine water and is combined with a rope impregnating machine or open width machine so as to form a closed system.

## Hollow Filaments

**Method for production of a hollow textile material.** Orlow William Boies and Harold Oliver Taylor (to Hartford Rayon Corp.). U. S. 2,379,783 (July 3, 1945).

Object of the invention is the production of a so-called hollow filament from viscose (having a multiplicity of voids). Method comprises preparing a solution containing an alkali metal hydroxide and a carbonate and then admixing a coagulable material belonging to the group consisting of cellulose esters and a cuprammonium solution of cellulose therein.

## Wool-Like Fibers

**Process for producing potentially adhesive textile fibers.** Roger Wallach (to American Viscose Corp.). U. S. 2,379,264 (June 26, 1945).

A general object of the invention is to produce a cellulose ether in the form of separable fibers of textile-making length, which are suitable for use in the textile and cordage arts. The fibers have a substantial curl, which imparts to the fibers a wool-like character.

## Electrically Heated Fabric

**Electrically heated fabric.** James A. Hendley (to The Russell Mfg. Co.). U. S. 2,379,580 (July 3, 1945).

The object of the invention is to provide an improved electrically heated fabric which can be manufactured in any desired length and which can afterward be cut into shorter lengths for making it into garments or for other uses. It is also intended that the fabric can readily be manufactured on looms and other fabric-making machinery. It is designed to give great flexibility and to have elastic properties.

## Knit Fabric

**Knit fabric and method of making the same.** Max Nebel (vested in Alien Property Custodian). U. S. 2,379,649 (July 3, 1945).

The object of the invention is to combine the principal advantages of warp goods and hosiery and to produce a new fabric having the characteristic features of warp goods as well as hosiery.

**Control of elasticity in knitted fabrics.** Vincent Lombardi (to Lombardi Knitting Machine Co., Inc.). U. S. 2,378,780 (June 19, 1945).

The invention relates to the use of elastic yarn in knitted fabrics in such a manner as to give considerable stretchability up to a certain point but not beyond that point; also to be able to give some control of elasticity to give further stretch in one direction than in another.

## Laminated Fabrics

**A stiffened, shaped, laminated fabric, possessing unusual elasticity.** Louis Glass (to Celanese Corp. of America). U. S. 2,377,933 (June 12, 1945).

The structure requires at least one of the layers to be made of or to contain a thermoplastic material. The construction involves a special method of cutting or folding the fabrics of which the laminate structure is composed. The result is a fabric of predetermined shape for uses such as sweat-bands for hats.

## Crinkled Synthetic Fibers

**Crinkled polymeric vinylidene chloride fibers.** William B. Robbins (to Dow Chemical Co.). U. S. 2,377,810 (June 5, 1945).

A process is described for the preparation of filaments, fibers, yarns, and fabrics resembling wool from vinylidene chloride.

## Non-Felting Wool

**Process for rendering wool non-felting.** Frederick A. Hessel and John B. Rust (to Ellis-Foster Co.). U. S. 2,382,632 (Aug. 14, 1945).

The process described consists of treating wool (either as the raw wool, yarn, knit, or woven goods) in an aqueous bath containing from 1 to 10% of a water-soluble basic nitrogen compound at temperatures usually ranging from 50° to 90°C and at atmospheric pressure or higher, depending upon the volatility of the compound. When wool is treated in this manner for periods varying from 15 min. to 1 hr., then rinsed and dried, its properties have been altered to such a degree that it no longer has a tendency to felt during washing and consequently is non-shrinking also. It has been found that various types of basic nitrogen compounds are suitable for this purpose: water-soluble primary and secondary amines, compounds of analogous basic nature such as hydroxylamine, hydrazine, semicarbazide, guanidine, and the like; tetraethanolammonium hydroxide, tripropanolethanolammonium hydroxide, and other mildly basic quaternary ammonium hydroxides which do not have a dissolving action on the wool; alkali salts of amino acids such as sodium aminoacetate and the salts of the amino acids of proteins. Ammonium carbonate is moderately effective but shows best results when used in combination with one of the other nitrogen compounds.

## Pigment Manufacture

**Manufacture of phthalocyanine pigments.** William B. Reynolds and Sylvester A. Scully (to Interchemical Corp.). U. S. 2,382,441 (Aug. 14, 1945).

A violently exothermic reaction as well as uneconomical loss of solvents (polyalcohols and polyethers), difficulties encountered in earlier methods of preparing phthalocyanine pigments, are avoided by the use of limited quantities of water-miscible hydroxy aliphatic solvents such as glycol, glycerol, polyglycols, etc., in the reaction between an aromatic ortho dinitrile and a metalliferous compound—e.g., cuprous chloride or cuprous oxide. E. N. Harvey

## Application of Adhesives

**Web pasting apparatus.** Russell J. Williams (to Bemis Bro. Bag Co.). U. S. 2,382,929 (Aug. 14, 1945).

Among the several objects of the invention are the provision of web pasting apparatus which lays on a clean-cut pattern of adhesive with any desired practical thickness of adhesive; and the provision of apparatus of this class which by means of a fairly simple construction is adaptable to produce variable pattern lengths on the web from which variable-sized blanks may be produced for various purposes.

## Radiant Heat Carbonizing

**Carbonizing cloth by use of infra-red heat.** Walter Ridley (to Riggs & Lombard, Inc.). U. S. 2,379,653 (July 3, 1945).

In an improved procedure for continuous carbonizing of woolen piece goods it is said that temperatures well above 300°F, including as high as 600°F, can be used effectively. Cloth is in contact with the heat for a period of the order of 15 secs. and the cloth itself is said to remain below 300°F. In the apparatus described the cloth is passed between banks of infra-red bulbs.

## Thermoplastic Coating

**Apparatus for smoothing thermoplastic coating materials.** Arthur M. Wickwire, Jr. (to Interchemical Corp.). U. S. 2,381,942 (Aug. 14, 1945).

Smoothing of thermoplastic or hot melt coatings by applying a high-temperature flame directly upon the coated surface of a traveling web, followed by treatment with a smoothing bar, and finally by a second direct heating of the coated surface is an improvement over the previous use of only a heated smoothing bar. The apparatus described is said to permit web speeds of 350 ft. per min. for viscous materials with high melting points and speeds up to 700 ft. per min. if the melting point is comparatively low. E. N. Harvey

## Textile Finishing

**Textile finishing treatment.** Wilbur N. Oldham (to American Cyanamid Co.). U. S. 2,378,724 (June 19, 1945).

An improved water-resistance, a more desirable hand, and an improved resistance against shrinking are said to result from the use of the method described. This method employs the use of a compound containing substantial amounts of a monoacyl guanidine in which the acyl group is a fatty acid radical containing at least 7 carbon atoms and also containing substantial amounts of a curable acid-curing thermosetting aminoplast resin, curing the resin on the fibers.

## Finishing Process

**Process for producing pattern effects on fabrics.** Georges Heberlein and Ernst Weiss (to Heberlein Patent Corp.). U. S. 2,382,416 (Aug. 14, 1945).

The invention relates to improved processes for finishing fabrics containing cellulose fiber, wherein certain areas according to a desired pattern are given a parchmentizing or transparentizing treatment, and also wherein certain areas of such pattern have applied thereto a pigment-containing resist of such character as to permanently remain in the fabric, and subsequently the fabric or portions of such pattern thereof are subjected to a shrinking treatment such as to give a pronounced difference in the appearance of the compactness of the weave, and, if desired, also to cause various undulated or cockled effects to ap-

pear in the different areas of the pattern.

## Fireproofing Compounds

**Fireproofing of textiles.** Martin Leatherman. U. S. 2,378,714 and 2,378,715 (June 19, 1945).

A fireproofing composition that is essentially a mixture of thermally unstable chlorinated resinous organic material, zinc carbonate, and monocalcium chlorophosphate, a wetting agent for the solid ingredients, a dispersion medium, and a plasticizer having fire-retarding properties.

## Insolubilizing Proteins

**Process of insolubilizing protein and product.** Ralph K. Iler (to Du Pont) U. S. 2,381,752 (Aug. 7, 1945).

A soluble protein may be insolubilized and rendered hydrophobic by the process described in this patent. The process involves mixing the protein in water solution with a water-soluble Werner complex which consists of a trivalent nuclear chromium atom coordinated with carboxylic acido groups containing at least 10 carbon atoms. Upon heating this mixture, it becomes irreversibly dehydrated and a chromium protein complex is formed which is insoluble and hydrophobic. The material may be dehydrated after application to a textile or paper to obtain an insoluble and hydrophobic coating, or it may be prepared in the form of a film or fiber. In the disclosure, an example specifies the use of animal glue with stearato chromic chloride. It is further disclosed that this Werner complex acts as a dispersing agent for paraffin wax so that highly water-repellent coatings can be obtained by addition of this ingredient.

A. R. Martin

## Rotproofing Treatment

**Treatment of textiles.** Carroll A. Hochwalt (to Monsanto Chem. Co.) U. S. 2,381,852 (Aug. 7, 1945).

Textiles may be simultaneously rotproofed and made water-repellent by treatment with the copper salt of a mono alkylene succinic acid, the alkylene substituent containing from 5 to 16 carbon atoms. The textile is treated with the soluble sodium salts of these acids and the insoluble copper salt formed by subsequent treatment with cupric acetate and drying. Data are given in the patent disclosure relative to the degree of rotproofness and water-repellency achieved by use of triisobutylene succinic anhydride and cupric acetate.

A. R. Martin

## Surface-Active Agents

**Wetting and emulsifying agents.** Kathryn L. Lynch and Herbert J. West (to American Cyanamid Co.). U. S. 2,379,535 (July 3, 1945).

The process for the production of dioctyl *N*-(beta-sodium sulfo ethyl) aspartate, which comprises reacting beta-sodium sulfo ethyl amine with dioctyl maleate. The compounds described in the patent are said to have wetting, dispersing, foaming, detergent, and other useful surface-active properties.

## Textile Treatment

**Improvement of wet strength of yarns, cords, and other textiles.** Robert Wighton Moncrieff and Harold Bates (to British Celanese, Ltd.). U. S. 2,379,026 (June 26, 1945).

The treatment is applicable to cellulose textiles either natural or regenerated. It is said to increase water resistant properties as well as improve the wet strength. The process consists principally of treatment in a non-solvent medium, consisting of the mixture of an ester of an acid having the formula $CH_3(CH_2)$-*n*-COOH where *n* is at least 4 and an anhydride of a saturated monocarboxylic containing more than one and fewer than 5 carbon atoms dissolved in a solvent, the reaction being continued until the weight of the materials has increased by at least 5%.

## Storage of Fabrics

**Protective casing for textiles by the yard.** William Polgar. U. S. 2,382,332 (Aug. 14, 1945).

An improved safety container for yard goods is described. It has fireproof, smokeproof, and dustproof features, and is so constructed that the fabric may be easily withdrawn and returned into the container. It is intended to be of assistance in the merchandising of textile piece goods.

## Textile Printing

**Textile printing compositions.** John R. Abrams (to Interchemical Corp.). U. S. 2,381,868 (Aug. 14, 1945).

In textile printing the reproduction of very fine designs, as from a photogravure cylinder, presented difficult problems before the introduction of textile printing pastes (Jennett, U.S. 2,222,581) based on emulsions of pigments in binders with a thermosetting resin component. Abrams claims improvement in wash-fastness of such compositions by the use of formulations which include a carbamide-formaldehyde resin (1 to 4 parts; 2 to 3 parts give optimum effect) plasticized with the methyl ester of abietic acid (1 part).

E. N. Harvey

**Textile printing pastes and textiles produced therefrom.** Norman S. Cassel (to Interchemical Corp.). U. S. 2,381,878 (Aug. 14, 1945).

In addition to crocking, "hand," and adhesion difficulties, textile printing pastes containing emulsified pigment-resin combinations sometimes show after application poor resistance to washing and dry-cleaning. Typical are compositions containing cellulose ethers. Cassel has discovered that small quantities of urea-formaldehyde resins (1 to 20 parts) may be blended with organic solvent-soluble cellulose ethers (20 parts) printing compositions (particularly with ethyl cellulose as binder) to give mixtures for application which show unusual resistance to washing and dry-cleaning solvents after the urea resin has been converted to the insoluble state.

E. N. Harvey